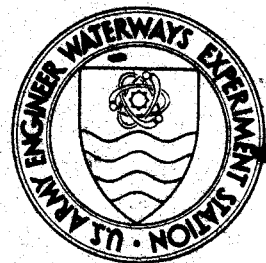


DREDGED MATERIAL RESEARCH PROGRAM



CONTRACT REPORT D-76-9

ABATEMENT OF MALODORS AT CONFINED DREDGED MATERIAL DISPOSAL SITES

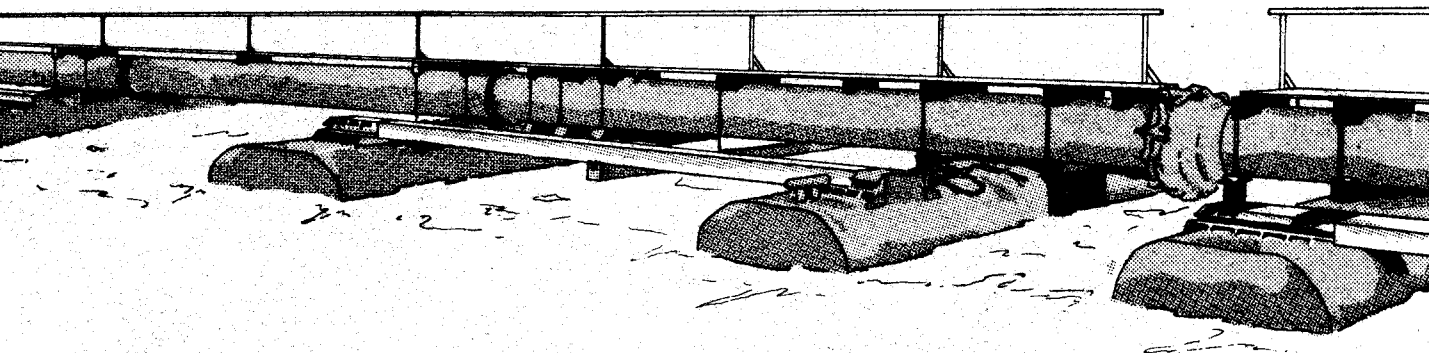
by

W. Harrison, A. Dravnieks, R. Zussman, R. Goltz
Argonne National Laboratory
Argonne, Illinois 60439

August 1976

Final Report

Approved For Public Release; Distribution Unlimited



Prepared for Office, Chief of Engineers, U. S. Army
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Monitored by Environmental Effects Laboratory
U. S. Army Engineer Waterways Experiment Station
P. O. Box 63 I, Vicksburg, Miss, 39180

Under Interagency Agreement No. WESRF 75-104
(DMRP Work Unit No. 2C1 I)

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Errata Sheet

No. 1

ABATEMENT OF MALODORS AT CONFINED DREDGED MATERIAL DISPOSAL SITES

Contract Report D-76-9

August 1976

1. The second page of the Form 1473 should read:

20. ABSTRACT (Continued)

forced-choice-triangle olfactometer. Although significant problems with malodors were not observed beyond the disposal area dikes during site visits, noteworthy odor episodes had occurred at some sites. An odor-abatement strategy is presented for handling the expected range of odor conditions at dredged material disposal sites. Its aim is to reduce to an acceptable level the perceived intensity of malodors in an affected community. The main steps in the strategy cover (1) selection of the disposal site, (2) site preparation, (3) odor characterization of sediments to be dredged, (4) malodor abatement during dredging and disposal operations, (5) malodor abatement after filling of the disposal site, and (6) the handling of malodor complaints.



DEPARTMENT OF THE ARMY
WATERWAYS EXPERIMENT STATION. CORPS OF ENGINEERS
P. O. BOX 631
VICKSBURG. MISSISSIPPI 39160

IN REPLY REFER TO: WESYV

30 August 1976

SUBJECT: Transmittal of Contract Report D-76-9

TO: All Report Recipients

1. The contract report transmitted herewith represents the results of one research effort (work unit) initiated as part of Task 2C (Containment Area Operations) of the Corps of Engineers' Dredged Material Research Program (DMRP). Task 2C is included as part of the Disposal Operations Project (DOP) of the DMRP, which, among other considerations, includes research into various ways of improving objectionable environmental conditions associated with the confined disposal of dredged material.
2. Confining dredged material on land is a relatively recent disposal alternative to which practically no specific design, construction, operation, or aesthetic improvement investigations, much less applied research, have been addressed. There has been a dramatic increase in the last several years in the amount of land disposal necessitated by confining dredged material classified as polluted. Confining material on land may alleviate some environmental problems associated with open-water disposal but in turn creates new environmental problems at confined disposal sites. Therefore, attention is being directed toward identifying and then improving adverse environmental situations at confined dredged material disposal areas.
3. DMRP work units are in progress to develop methods for eliminating or mitigating objectionable environmental conditions at disposal areas. One objectional condition often mentioned is malodors that on occasion are associated with containment areas. The investigation reported herein was accomplished by Argonne National Laboratory to develop abatement procedures for malodors.
4. Numerous samples of air and dredged material were collected from seven confined disposal sites located throughout the United States. Quantitative and subjective laboratory tests were performed to identify and characterize various odors encountered. Significant malodor problems were not encountered during the study, but noteworthy odor episodes had occurred at some sites. An odor abatement strategy was developed that consists of a series of management decisions including disposal site selection, site preparation, odor characterization of the sediment to be dredged, odor abatement during dredging and disposal operations, malodor abatement after disposal, and handling of odor complaints.

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5. This study is considered to be a significant contribution to a solution of the problem of the elimination or mitigation of malodors associated with confined disposal areas. The guidelines presented herein are implementable now and Corps operating elements are encouraged to seek opportunities to apply them. Because of the almost nonexistent state-of-the-art in field-tested and operationally proven malodor abatement methodologies, the performance data resulting from field applications will be quite valuable in technique refinement and determination of limits of applicability.

A handwritten signature in cursive script, appearing to read "John Cannon".

JOHN L. CANNON

Colonel, Corps of Engineers
Commander and Director

Unclassified

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10. ABSTRACT (Continue on reverse side if necessary and identify by block number) Samples of malodorous air and dredged material were collected during the period July-October 1975 at confined disposal sites at the following locations: Buffalo, N. Y., Milwaukee, Wis., Mobile, Ala., York Harbor, Maine, Houston, Tex., Detroit, Mich., and Anacortes, Wash. Odorous compounds in the air samples were identified by gas chromatography/mass spectrometry, while the detection threshold, intensity, and character of the various odors were determined by experienced odor panelists using a dynamic, (Continued)		

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20. ABSTRACT (Continued)

and granular media cartridges), and a general methodology for the design of containment facilities as solid-liquid separation systems was formulated.

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EXECUTIVE SUMMARY

This report presents the results of research conducted by Argonne National Laboratory (ANL) for the Disposal Operations Project of the Dredged Material Research Program (DMRP) of the U.S. Army Engineer Waterways Experiment Station. The objective of the DMRP is to provide more definitive information on the environmental aspects of dredging and dredged material disposal operations and to develop technically satisfactory, environmentally compatible, and economically feasible dredging and disposal alternatives. During 1975, an ANL research team visited seven Corps' disposal sites where malodors had been or were expected to be objectionable; six of the sites were actively being filled. The sites represented a range of odor-producing conditions; none, however, exhibited the intensities of malodor production reported to have occurred in the past. Nevertheless, considerable data related to the odors present were gathered and these data are presented in 38 tables.

The present study emphasized the following items and drew the following conclusions:

- a. Characterization of perceived odors and magnitude of odor emissions at disposal sites

Samples of ambient air and dredged material were collected at each site and evaluated by a nine-person odor panel in terms of odor-dilution thresholds and odor types. Threshold values were compared to typical odor-control regulations. The results showed that the potential for malodor complaints at all seven sites was low and that in most cases even the strictest of existing regulations would not be violated. Reduction of odor intensity by a factor of only 2 or 3 would bring all cases within acceptable limits.

b. Identification of volatiles causing odor problems at dredged material sites

Malodorous vapors were collected at each disposal site and identifications of the contained organic compounds were made by gas chromatography/mass spectrometry (GC/MS). Odorograms were also prepared by using a GC equipped with a sniffing port and standard and sulfur-specific columns. The amount of hydrogen-sulfide gas was determined at each site with a special detector.

c. Determination of sources and causes of odor problems

Gases liberated during pumpout were found to be the primary source of malodors. The principal, volatile malodorous compounds originated from dredged material contaminants (such as petroleum-derived compounds) or from the biogenic production of sulfur compounds. A second source of malodors at some sites was the continued release, by *de novo* synthesis, of volatile malodorous compounds from the disposed dredged material.

d. Investigation of methods for abatement of odors

Approaches in use in Europe and Australia for control of odors associated with dredging activities were canvassed. It was found that significant odor problems have occurred primarily when chemical wastes were present in the sediments being dredged. In the Netherlands, the odor problem was overcome by abandoning all dredging of such contaminated sediments. Odor counteractants have been employed in Great Britain, but the results are poorly documented.

Odor control by a counteractant is practiced at the Clinton disposal site in Houston, Texas. Odor-panel tests showed no reduction in odor intensity at the Clinton site, but there was a slight change in odor character. The odor-counteraction and odor-modification approaches to abatement of malodors require careful study prior to the adoption because of a lack of technical data on their effectiveness

and safety. With regard to the use of oxidants for source modification, potassium permanganate, hydrogen peroxide, and sodium hypochlorite reduced the intensities of malodors from a dredged material sample by a factor of 2 to 3 in small-scale laboratory tests. Addition of lime is used in Sweden and could be considered, as well.

e. Guidelines for abatement of malodors

An odor-abatement strategy is presented in Figure 23 of the report. It involves a series of management decisions. Results of the decisions made in each step of the abatement strategy are evaluated in terms of their relative cost effectiveness. The management steps to be considered cover disposal site selection, site preparation, odor characterization of the sediments to be dredged, abatement of malodors during dredging and disposal operations, malodor abatement after filling of the disposal site, and the handling of complaints of malodors.

Complaints of malodors at diked dredged material disposal sites may be expected to occur **most-commonly** at the time that malodorous dredged material is pumped into a disposal site. Unpleasant odors decrease in intensity rapidly after placement of dredged material. A proportionally rapid decrease in the frequency of complaints may be expected after cessation of site filling. The most effective way to handle the potential of malodors is by advance implementation of the appropriate management steps as found in the odor-abatement strategy (Figure 23).

The physical setting of a disposal site, the nature of the materials to be dredged, and the local materials available for odor abatement together constitute a unique matrix that requires **specially-**devised management actions. It is not feasible to promulgate uniform guidelines or to write a manual of practice for odor abatement for the wide variety of diked dredged material disposal sites under jurisdiction of the Corps. Site-specific odor-abatement strategies can be developed, however, by following the guidelines of Figure 23.

PREFACE

The work described in this report was performed under Inter-agency Agreement No. WESRF 75-104 between the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, and Argonne National Laboratory (ANL), Argonne, Illinois. The research was sponsored by the Office, Chief of Engineers (DAEN-CWO-M), under the Civil Works Dredged Material Research Program (DMRP).

Malodors associated with confined dredged material disposal areas are sometimes the subject of public complaints. This report discusses the causes and treatment of objectional odor conditions in confined disposal areas and makes recommendations for odor abatement.

The work was conducted by W. Harrison, A. Dravnieks, R. Zussman, and R. Goltz of the Argonne National Laboratory. Assistance in the field sampling phase of the study was given by G. Greener of the Buffalo District, B. Bochantin of the Chicago District, F. Pruitt of the Mobile District, J. Gaster of the Detroit District, F. Ciccone of the New England Division, W. Hopkins of the Galveston District, and D. Mahan of the Seattle District. Mr. L. Van Loon, ANL, also assisted on two field trips.

Mr. R. Clas, of Robert S. Clas and Associates, Baltimore, Maryland, provided information on the operational aspects of dredged material disposal. Mr. O. Lauren, of O. M. Lauren Associates, La Grange, Illinois, provided information and advice on odor-modification procedures.

The report was prepared for the Disposal Operations Project (DOP) of the DMRP (C. Calhoun, Jr., Manager) as part of Task 2C "Containment Area Operations" (Mr. N. Baker, Manager). The contract was managed by Mr. Baker under the general supervision of Dr. J. Harrison, Chief, Environmental Effects Laboratory.

COL G. H. Hilt, CE, and COL J. L. Cannon, CE, were Directors of WES during the period of this contract and Mr. F. R. Brown was the Technical Director.

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CONVERSION FACTORS, U. S. CUSTOMARY TO METRIC (SI)
UNITS OF MEASUREMENT

The U. S. customary units of measurement used in this report can be converted to metric units as follows:

<u>Multiply</u>	<u>By</u>	<u>To Obtain</u>
inches	2.54	centimetres
feet	0.3048	metres
miles (U. S. statute)	1.609344	kilometres
square inches	6.4516	square centimetres
square feet	0.09290304	square metres
acres	4046.856	square metres
cubic feet	0.02831685	cubic metres
cubic yards	0.7645549	cubic metres
ounces	29.57353	cubic centimetres
gallons	0.003785412	cubic metres
pounds (mass)	0.4535924	kilograms
pounds (force) per square inch	6.894757	kilopascals
pounds (force) per cubic foot	0.1571	kilopascals per metre
horsepower	745.6999	watts

INTRODUCTION

Purpose and Scope of Study

The present study was designed to characterize the nature and determine the origin of odors at diked dredged material disposal sites and to make cost-effective recommendations for odor abatement. The field phase of the study was conducted during the period July 2 to October 1, 1975. During this period, a total of seven sites were found with sufficient odor problems to warrant sampling trips. Although the scope of the study was somewhat restricted as to the number of sites, a reasonable range of odor-producing situations were visited. Samples were obtained from the following locations on the Atlantic and Pacific coasts, near the Gulf of Mexico, and along the shores of the Great Lakes: Buffalo, New York; Milwaukee, Wisconsin; Mobile, Alabama; York Harbor, Maine; Houston, Texas; Detroit, Michigan; and Anacortes, Washington.

Approach

A laboratory program of odor analysis was adopted. Several samples of odorous air were taken at each field site. Air samples were pumped into plastic bags and flown back to the laboratory for determination of odor type and intensity by experienced odor panelists. Other samples were taken by pumping odorous air through specially designed collectors. These samples were analyzed for organic compounds in an effort to make thorough chemical characterizations of the odorous substances. Finally, bacteriological samples were taken at each dredged material site in an effort to determine if specific bacteria were contributing significantly to the measured odors.

With regard to odor abatement, it was decided to approach the problem both experimentally and by canvassing state-of-the-art methods. The effect of a variety of oxidizing agents on reduction

of odor intensity was examined using odor panelists. At the same time, several telephone, written, and face-to-face interviews were conducted with individuals either knowledgeable about odor modification and odor masking or familiar with dredging and disposal procedures likely to contribute to the reduced liberation of odorous gases.

Previous Work

The authors were unable to find any published work dealing specifically with the characterization or generation of odors at confined (or unconfined) dredged material disposal sites. However, a short memorandum report was developed for the District Engineer, Chicago District, U.S. Army Corps of Engineers (1972), entitled "Abatement of Objectionable Odors Produced by Contained Dredge Spoil." This report was only a brief review of the problem with recommendations for the development of Corps' programs in odor abatement. No measurements of any kind were taken.

Odor-abatement procedures used by the Galveston District are mentioned briefly in Murphy and Zeigler (1974, p. 60). The procedures involve the use of (1) kerosene, containing a masking agent, for odor abatement at the Houston Ship Channel maintenance dredging disposal sites and (2) the use of an odor counteractant and constricted sluices at the Clinton disposal area in Houston itself. The sluices (Murphy and Zeigler, 1974, Figure 22) were designed to prevent turbulent flow of the effluent out of the diked area, thereby reducing emission of odors.

SAMPLING METHODS

Air Samples

Chromosorb collectors

These devices have been described by Dravnieks et al. (1971). A collector consists of a stainless-steel cylinder containing five grams of Chromosorb 102, a high-surface-area, styrene-divinyl-benzene copolymer compound. Chromosorb 102 is nonpolar, absorbs little water vapor, and because of its large surface area ($300\text{--}400\text{ m}^2/\text{g}$), is an excellent absorber of organic vapors. The air to be sampled is pumped through one or more of these collectors for 30 minutes, at a flow rate of 1.67 l/min . This results in the entrapment of the organic species contained in approximately 50 l of air.

At each of the seven sampling sites, four samples were collected simultaneously, by means of a glass-manifold, pump, and flowmeter assembly. Prior to each sampling period the collectors were purged overnight with a pure helium flow of 60 ml/min , at 120°C . Samples were taken while dredged material was being discharged and at a location as close as possible to the outfall end of the pumpout pipe. Immediately after a sampling run, the collectors were disconnected and sealed with Swagelock fittings. These units were then stored in a cool place until the gas chromatograph/mass spectrometer (GC/MS) was available, usually 1 to 3 days after a sampling run.

Tedlar-bag collectors

Bags of approximately 18-R capacity were manufactured for the taking of air samples for use with an experienced group of panelists. Two sheets of 0.003-in.-thick Tedlar film were heat sealed to form a flat bag 12 by 32 in. in size with a 2-in.-long spout to accept 0.25-in. O.D. stainless steel tubing.* A short length of the tubing was inserted into the spout and fastened with electrician's tape.

*A table of factors for converting U. S. customary units of measurement to metric (SI) units is presented on page 15.

Samples of ambient air were taken (Dravnieks, Prokop, and Boehme, 1975) by placing the bags into an aluminum drum equipped with a flange and a **0.75-in.-thick** Plexiglass end plate. The end plate was attached to the cylinder's flange. The plate was provided with a central spout for insertion of the bag's stainless steel tubing and with a nipple carrying a needle valve. The drum was 9 in. O.D., weighed 20 lb, and was easily portable. A short piece of latex rubber tubing was used to hold the bag's tubing in the spout.

To sample in the field, a hand-operated neoprene bellows pump* was used to extract air, via the top plate nipple and valve, from the space between the cylinder and the bag. The bag inflates, taking a sample through its stainless tubing. Pre-flushing the bag was necessary to reduce odor losses by sorption at the bag walls. This was done by taking several liters of ambient air into the bag, followed by reversing the hand pump and expelling the sample by compressing the bag. The pump was again reversed, and the actual sample was taken. The entire procedure took 2-3 minutes. The sample was sealed by a latex rubber tube plugged with a short piece of glass rod. If another sample were to be taken, the end plate would be removed; the tubing spout of the bag would be rapidly pulled out from the end plate and immediately sealed as above; and a new bag would then be attached.

Samples were evaluated within 24 hr after sampling. Previous work (Dravnieks, Prokop, and Boehme, 1975) has shown that odors do not deteriorate significantly in storage of this duration.

Dredged Material Samples

About 100 ml of freshly disposed dredged material were collected at each site, placed in a glass jar, and flown to the odor panel for evaluation within 24 hr. The odor intensity of the dredged material

*Guzzler, Cole-Palmer Go., Chicago.

was greater than that of the ambient air; this permitted the odor panelists to better describe the odor characteristics of each sample.

A special three-gal. sample of dredged material was collected at the Detroit diked disposal site and stored at 4°C to retard biological activity. This sample was used to test the efficiency of oxidants in reducing odor threshold and odor intensity.

Bacteriological Samples

Field procedures

Where possible, solid or semisolid dredged material was chosen for bacteriological sampling, as opposed to highly aqueous suspensions of the material. At sites where the composition of dredged material issuing from the discharge pipe was visually judged to contain too much water, recently-discharged and partially-dessicated material was chosen for sampling at an area close to the outlet of the discharge pipe.

A clean, long-handled cooking spoon was employed to remove the uppermost dredged material, in several passes, until a depth of approximately 12-15 cm was reached. The next layer, approximately 4-cm thick, was deposited upon a sheet of clean paper and was bisected with two sterile pipettes in order to expose the inside. Using the rims of sterile plastic tubes as scoops, 5 to 10-gm samples were transferred to each of four tubes. These tubes were then capped and tightly taped. A sterile nichrome bacteriological loop was used to transfer additional material to various bacteriological media.

When high-water-content dredged material was sampled directly from the mouth of a discharge pipe, grab samples were obtained with propipette-outfitted sterile plastic pipettes of 10-ml capacity. Five 5-ml samples were expelled into separate sterile plastic tubes,

four of which were capped and taped. The fifth sample was retained for immediate aseptic transfer to bacteriological media.

Dredged material samples at all sites were immediately inoculated into BBL* Prepared Thioglycollate Medium and streaked for isolation onto BBL prepared trypticase soy agar plates. One exception was the substitution of Mueller-Hinton and blood agar plates for trypticase soy at the Anacortes, Washington, site. A sample of approximately one-half gram was estimated for inoculation into the thioglycollate tubes.

Storage and incubation

In the early stages of this study, two samples of dredged material from each site were transferred to Dewar bottles containing either frozen carbon dioxide or water ice. Following initial transport from the site, the dry ice samples were kept at freezer temperatures (approximately -25°C or below) until bacteriological analysis was performed. Water-ice samples were kept at refrigerator temperatures until workup. Frozen storage was immediately discontinued in favor of storage at refrigerator temperatures when it was discovered that bacterial viability was greatly decreased by freezing.

Immediately after inoculation with dredged material, the thioglycollate tubes and petri dishes were placed into a BBL GasPak for anaerobic growth. Such cultures were incubated at room temperature for approximately 48 to 72 hr or until adequate colonial growth was observed on the dishes through the side of the GasPak. Further growth was then inhibited by placing the unopened GasPak assembly in the refrigerator for storage.

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Ancillary Environmental Data

Several measurements of ambient conditions were made at each diked disposal site during the time that the Chromosorb- and Tedlar-bag collectors were being filled. The H_2S content of the air near the end of the discharge pipe was measured with a lead acetate detector (Metronics Associates Model No. 721). Wind speed was determined at a point 1.5 m off the ground with a hand-held cup anemometer. Wind direction was estimated using a hand-held compass and relative humidity was determined with a sling psychrometer. Air temperature and dredged material temperature were determined with a mercury stem thermometer. Dredged material pH was determined with Fisher Alkacid pH paper that had a pH range from 2 to 10. The general odor type was estimated by the scientists present in a given sampling party.

SAMPLE ANALYSIS

Identification of Odorous Compounds

Identification scheme

Odorous compound identification was accomplished by human nose and by gas chromatography/mass spectrometry (GC/MS). One of the four Chromosorb samples from each site was analyzed on a Hewlett-Packard GC/MS system located at Northwestern University. Two of the Chromosorb samples were analyzed on a Varian Aerograph GC at the Illinois Institute of Technology Research Institute (IITRI). One Chromosorb-collected sample was held as a backup in case of an analytical failure at either institution.

Both the Northwestern and the IITRI gas chromatographs were equipped with Supelco SP-1000 columns of 1/8-in. O.D. These GC's were temperature programmed at 45-180°C at 2°C/min. In addition, the SP-1000 column at IITRI was exchanged for a sulfur-specific (acidified polyphenyl ether) column for running the second Chromosorb sample. The IITRI GC was equipped with a sniffing port so that a notation could be made by the operator of the GC concerning the odor characteristic (if present) while a given peak was being recorded on a chromatogram. (The IITRI GC was used because the Northwestern GC did not have a sniffing port or a sulfur-specific column.)

The scheme for identification of odorous compounds, then, involved relating the odorous peaks (Figure 1) found using IITRI's SP-1000 column and sniffing port to the same peaks found using Northwestern's SP-1000 column and GC-coupled mass spectrometer. Thus, from among the many compounds that might be identified in a sample through the use of Northwestern's GC/MS, it would be possible to pick out those which were, in fact, odorous. Although the foregoing scheme is reliable in principle, at times it was difficult to relate peaks from the IITRI GC to those from the Northwestern GC. This was believed to be due to the differing characteristics of the

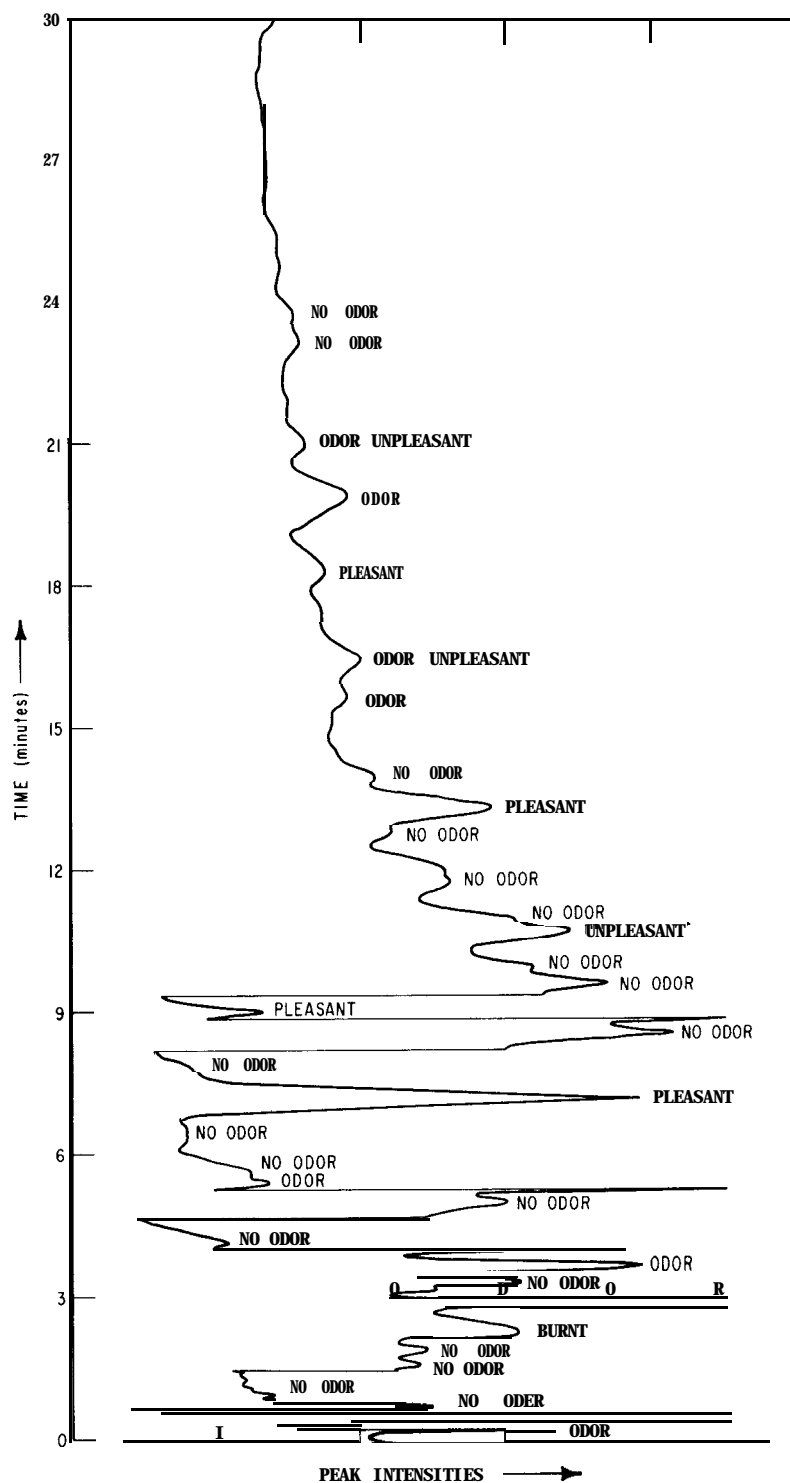


Figure 1. Typical odorogram obtained from IITRI gas chromatograph equipped with a sniffing port. Air sample was from Milwaukee Harbor.

SP-1000 columns and to unavoidable differences in the operational characteristics of flow and temperature programming controls for the two instruments. Northwestern's SP-1000 column was 12 ft long, with 2% loading, while IITRI's was a 10-ft-long column with 10% loading.

The difference between the data from two instruments is not critical. Compounds identified mass-spectrometrically did occur in the samples, but it was not always possible to indicate which peak in the odorogram corresponded to some specific compound so identified. Likewise, odors assayed in the odorograms did belong to the components of samples but sometimes could not be positively assigned to a specific mass-spectrometrically-identified component. Both methods essentially supplement one another.

Analytical details

Dravnieks et al. (1971, p. 1221) have described the injector needle and related apparatus used to elute the organic vapors off the Chromosorb and into the GC. The sample-injection apparatus had to be modified somewhat for Northwestern's GC, a Hewlett-Packard 5700 Series. Occasionally, loss of material was noted during the injection of a sample into the GC at Northwestern. This resulted in a reduced peak size and often made the interpretation of the mass spectra impossible, due to large background effects. Eventually, this phenomenon was traced to the length of time that the sample was heated. It was possible to correct for this problem by heating the needle for about one minute during injection.

In a typical run at Northwestern University, the GC column was programmed at 2°C per minute to 180°C and held at that temperature until no more components eluted from the column. Components injected on the column from the injector needle eluted from the outlet of the column at different intervals depending upon their adsorption on the liquid phase, SP-1000, and upon their vapor pressure. Thus, a separation or partial separation of each of the components of the

air sample could be achieved. A visual representation of such a separation is shown in Figure 2, where the time from the moment of injection, the retention time, is the x-axis and the amount of sample eluting from the GC column, as measured by a flame ionization detector hooked to the separator/enricher outlet, is along the y-axis. A portion of the components eluting from the column was sent to the mass spectrometer and mass spectra were run when desired. Since part of the liquid phase of the column also enters the mass spectrometer along with each component of air, background mass spectra were run from time to time between peaks. Those mass-spectral peaks associated with the background were subtracted from the mass spectra obtained at the time that a component of the air sample was eluting from the column.

A background-subtracted, or clean, mass spectrum is shown in Figure 3. It corresponds to GC peak "51-58" of Figure 2. The most intense peak in the spectrum of Figure 3 is m/e 77. The second most intense peak is m/e 105; the third is m/e 106; the fourth m/e 51; the fifth m/e 50; and the sixth, m/e 78. According to pre-existing lists of mass spectra (American Society for Testing and Materials, 1969), it can be concluded that the substance producing the original GC peak is benzaldehyde. All the mass spectra of this study were determined in this fashion. It was often impossible to determine the identity of a compound when the peaks of the mass spectrum were barely, if at all, above the peaks of the background; that is, when the compound was present only in trace amounts.

The sulfur-specific column used at IITRI was a Supelco, T/polyphenyl ether column (12% OS-124), containing 0.5% H_3PO_4 and 40/60 mesh Chromosorb. The SP-1000 column used was a 10-ft, 10% on 50/80 mesh Supelcoport column of 0.125-in. O.D. As mentioned earlier, the GC was a 1200 Series Varian Aerograph equipped with the sample-transfer apparatus described by Dravnieks et al (1971).

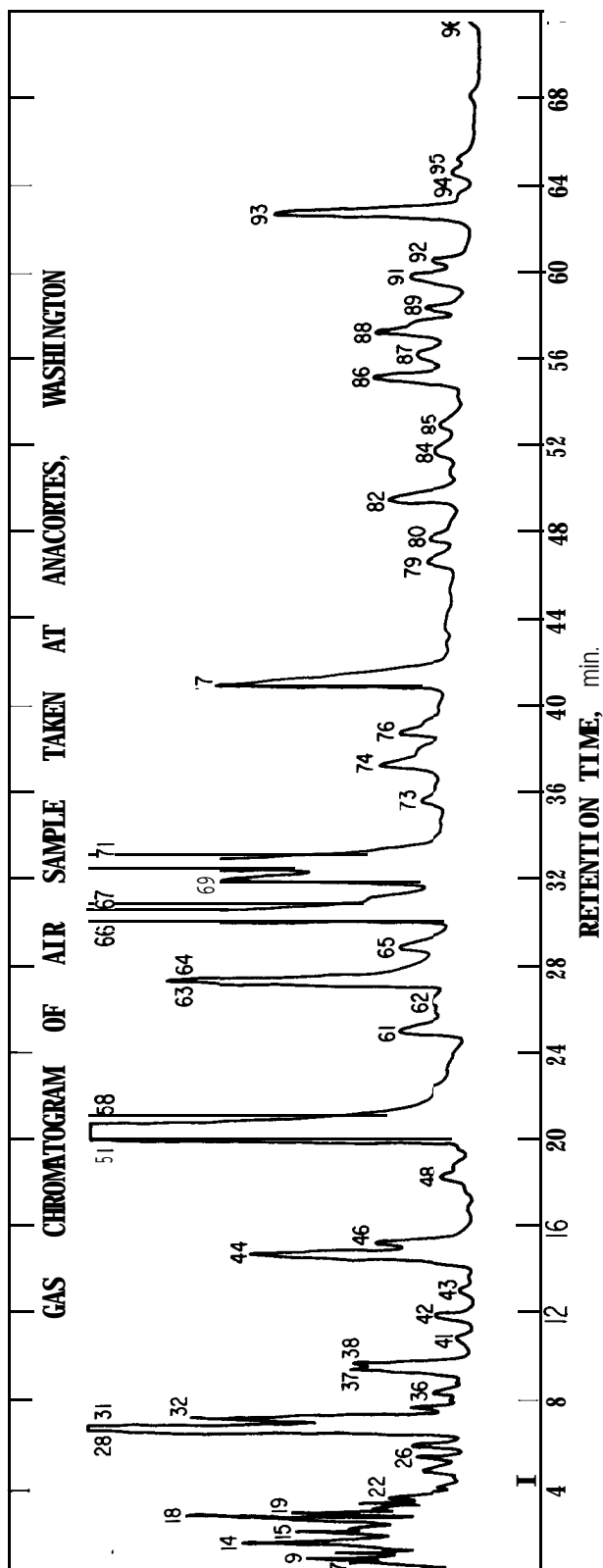


Figure 2. Typical gas chromatogram obtained from the gas chromatograph at Northwestern University. Numbers above each peak indicate that a mass spectrogram was taken for that peak.

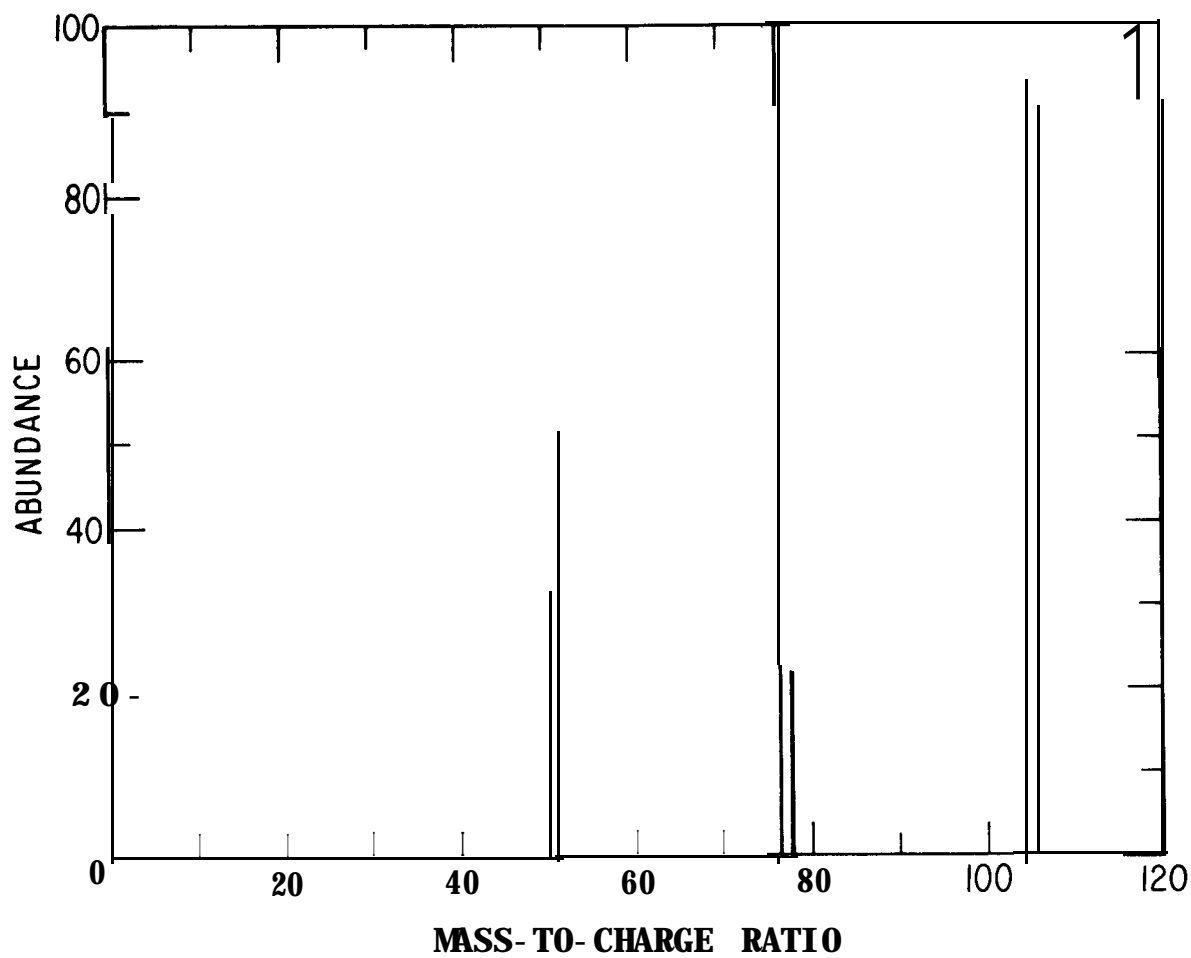


Figure 3. Clean mass spectrum for benzaldehyde, corresponding to GC peak 51-58 of Figure 2.

Determination of Odor Properties

The principal dimensions of an odor are its detection threshold, intensity, and character. In odorous air pollution measurements, the detection threshold is traditionally defined in terms of the American Society for Testing and Materials (ASTM) odor units (American Society for Testing and Materials, 1967). The form of definition is presently undergoing a revision; essentially, the numerical value in odor units indicates the extent of dilution with nonodorous air needed to reach an odor detection threshold. Thus, one volume of odorous air that is 12 odor units strong needs an additional 11 volumes of odorless air (to produce a total of 12 volumes) to obtain a diluted sample with an odor that 50% of the panelists on an odor panel would, and the other 50% would not, find odorous.

Odor intensity is only loosely related to the odor-unit content of an odorous air sample. Odor intensity S is the intensity of the odorous sensation (American Society for Testing and Materials, 1975) and increases with the concentration of **odorants** in accordance with a function

$$S = kC^n$$

where C is the concentration of the **odorants** in the sample, for instance in odor units, and k and n are coefficients that are different for different odorants.

Therefore, odor-unit content is not a direct measure of the odor intensity of the undiluted sample; rather, it indicates simply the extent of dilution needed to make a sample reasonably odorless. One odor at 12 units may actually smell considerably stronger or weaker than another odor, also 12 odor units strong.

This problem is handled by a new ASTM Tentative Procedure for Referencing Odor Suprathreshold Intensity (E-544), which uses a 1-butanol concentration scale to reference the nondiluted odor

intensity (American Society for Testing and Materials, 1975). This method for measuring undiluted odor intensity, however, has not yet become part of any regulations.

Since the only experience published and reflected in various odor-control regulations is anchored to the odor-unit concept, the odor-unit content of the Tedlar-bag samples was evaluated using the procedure described below. The procedure based on the new ASTM E-544 procedure was not used because not enough data exist to interpret the environmental significance of E-544 intensity values.

The other important dimension of odor is its character. The multidescriptor scale, developed by Harper et al. (1968) and consisting of 44 descriptors, has been expanded recently by Dravnieks, O'Donnell, and Reilich (1975) to include 136 descriptors (Table 1), to provide a better resolution of odor character. Panelists smell the sample and give their estimates of the degree of applicability of each odor descriptor using a score scale of 0 to 5. The result is a multi-dimensional profile of the odor. The meaning of the scale points (Table 1) is as follows:

0	=	described	quality	absent
1	=	described	quality	slightly applicable
2	=	"	"	"
3	=	described	quality	moderately applicable
4	=	"	"	"
5	=	described	quality	extremely appropriate

Determination of the odor properties was conducted at the IITRI Sensory Research Facility in Park Forest, Illinois. Samples collected in the field trips were evaluated within 24 hr after collection, using odor panels consisting of 9 experienced members. The panelists were not aware of the nature of the samples. Samples from the same field trip were evaluated by the same group in the same session, thus reducing the variability due to human factors. There was some unavoidable variation in the panel composition from session to session, but

Table 1

Odor Descriptor Form

	Absent 0	Slightly 1	Quality Scale										Extremely 5		
			2		3		4								
Fragrant		0	1	2	3	4	5	Oily, Fatty		0	1	2	3	4	5
Sweaty		0	1	2	3	4	5	Like Mothballs		0	1	2	3	4	5
Almond-like		0	1	2	3	4	5	Like Gasoline, Solvent		0	1	2	3	4	5
Burnt, Smoky		0	1	2	3	4	5	Cooked Vegetables		0	1	2	3	4	5
Herbal, Green, Cut Grass, etc.		0	1	2	3	4	5	Sweet		0	1	2	3	4	5
Etherish, Anaesthetic		0	1	2	3	4	5	Fishy		0	1	2	3	4	5
Sour, Acid, Vinegar, etc.		0	1	2	3	4	5	Spicy		0	1	2	3	4	5
Like Blood, Raw Meat		0	1	2	3	4	5	Paint-like		0	1	2	3	4	5
Dry, Powdery		0	1	2	3	4	5	Rancid		0	1	2	3	4	5
Like Ammonia		0	1	2	3	4	5	Minty, Peppermint		0	1	2	3	4	5
Disinfectant, Carbolic		0	1	2	3	4	5	Sulphidic		0	1	2	3	4	5
Aromatic		0	1	2	3	4	5	Fruit (citrus)		0	1	2	3	4	5
Meaty (cooked)		0	1	2	3	4	5	Fruity (other)		0	1	2	3	4	5
Sickening		0	1	2	3	4	5	Putrid, Foul, Decayed		0	1	2	3	4	5
Musty, Earthy, Moldy		0	1	2	3	4	5	Woody, Resinous		0	1	2	3	4	5
Sharp, Pungent, Acid		0	1	2	3	4	5	Musk-like		0	1	2	3	4	5

Table 1 (Cont'd)

	Absent 0	Slightly 1	Quality Scale					Extremely 5					
			2	3	4								
Camphor-like	0	1	2	3	4	5	Soapy	0	1	2	3	4	5
Light	0	1	2	3	4	5	Garlic, Onion	0	1	2	3	4	5
Heavy	0	1	2	3	4	5	Animal	0	1	2	3	4	5
Cool, Cooling	0	1	2	3	4	5	Vanilla-like	0	1	2	3	4	5
Warm	0	1	2	3	4	5	Fecal (like manure)	0	1	2	3	4	5
Metallic	0	1	2	3	4	5	Floral	0	1	2	3	4	5
Perfumery	0	1	2	3	4	5	Yeasty	0	1	2	3	4	5
Malty	0	1	2	3	4	5	Cheesy	0	1	2	3	4	5
Cinnamon	0	1	2	3	4	5	Honey-like	0	1	2	3	4	5
Popcorn	0	1	2	3	4	5	Anise (licorice)	0	1	2	3	4	5
Incense	0	1	2	3	4	5	Turpentine (pine oil)	0	1	2	3	4	5
Melony (cantaloupe, honey dew melon)	0	1	2	3	4	5	Fresh Green Vegetables	0	1	2	3	4	5
Tar-like	0	1	2	3	4	5	Medicinal	0	1	2	3	4	5
Eucalyptus	0	1	2	3	4	5	Strawberry-like	0	1	2	3	4	5
Buttery	0	1	2	3	4	5	Stale	0	1	2	3	4	5
Like Burnt Paper	0	1	2	3	4	5	Cork-like	0	1	2	3	4	5
Cologne	0	1	2	3	4	5	Lavender	0	1	2	3	4	5

Table 1 (Cont'd)

Absent 0	Slightly 1	Quality Scale													
		2		3		4		Extremely 5							
Geranium Leaves		0	1	2	3	4	5	Rubbery (new rubber)		0	1	2	3	4	5
Urine-like		0	1	2	3	4	5	Bakery (fresh bread)		0	1	2	3	4	5
Beery (beer-like)		0	1	2	3	4	5	Oak Wood, Cognac-like		0	1	2	3	4	5
Cedarwood-like		0	1	2	3	4	5	Grapefruit		0	1	2	3	4	5
Coconut-like		0	1	2	3	4	5	Grape-juice-like		0	1	2	3	4	5
Rope-like		0	1	2	3	4	5	Eggy (fresh eggs)		0	1	2	3	4	5
Seminal, Sperm-like		0	1	2	3	4	5	Bitter		0	1	2	3	4	5
Like Cleaning Fluid (Carbona)		0	1	2	3	4	5	Cadaverous, like Dead Animal		0	1	2	3	4	5
Cardboard-like		0	1	2	3	4	5	Maple (as in Syrup)		0	1	2	3	4	5
Lemon (fruit)		0	1	2	3	4	5	Seasoning (for meat)		0	1	2	3	4	5
Dirty Linen-like		0	1	2	3	4	5	Apple (fruit)		0	1	2	3	4	5
Kipperry (smoked fish)		0	1	2	3	4	5	soup		0	1	2	3	4	5
Caramel		0	1	2	3	4	5	Grainy (as grain)		0	1	2	3	4	5
Sauerkraut-like		0	1	2	3	4	5	Clove-like		0	1	2	3	4	5
Crushed Grass		0	1	2	3	4	5	Raisins		0	1	2	3	4	5
Chocolate		0	1	2	3	4	5	Hay		0	1	2	3	4	5
Molasses		0	1	2	3	4	5	Kerosene		0	1	2	3	4	5

generally, panel-averaged data did not grossly fluctuate (cf. Dravnieks, Prokop, and Boehme, 1975), because the policy used in forming the odor panels was to use substitutes that have approximately the same level of olfactory sensitivity as the missing members.

Odor units

The apparatus shown in Figure 4 was used to determine the dilution thresholds of the Tedlar-bag air samples. A bag containing the sample was placed in the drum and compressed, by pumping air into the space surrounding the bag. This expels the sample at a controlled rate, regulated by a water-column manostat, into a 5-level, dynamic-triangle olfactometer (Dravnieks et al. 1975). The sample was made available at a steady, continuous flow of 500 ml/min and at dilutions of 81x, 27x, 9x, 3x, and 1x (no dilution). At each dilution level, the panelist was also presented with ~~two~~ blank air samples (all flowing at 500 ml/min) and had to select, every time from the three ("triangle") samples presented, the odor that was different from the other two. The panelist signaled his selection by depressing the appropriate button, which produced a lighted signal on the scoreboard panel (Figure 4). The panelist had to make a choice; if he could not decide on the basis of odor, he had to simply guess. This was a basic requirement in the forced-choice-triangle procedure, and was necessary for statistical reasons.

Nine panelists were used, selected to represent approximately the distribution of the odor sensitivities in the general population (three high, three low and three of medium sensitivity). Each panelist began with the most diluted sample level (81x) and proceeded through the increasingly more concentrated samples. A panelist's detection threshold was defined statistically as the geometric mean of that dilution at which he missed last for the particular sample and that dilution beginning with which he began to select correctly and consistently. The panel-averaged dilution threshold is the geometrical

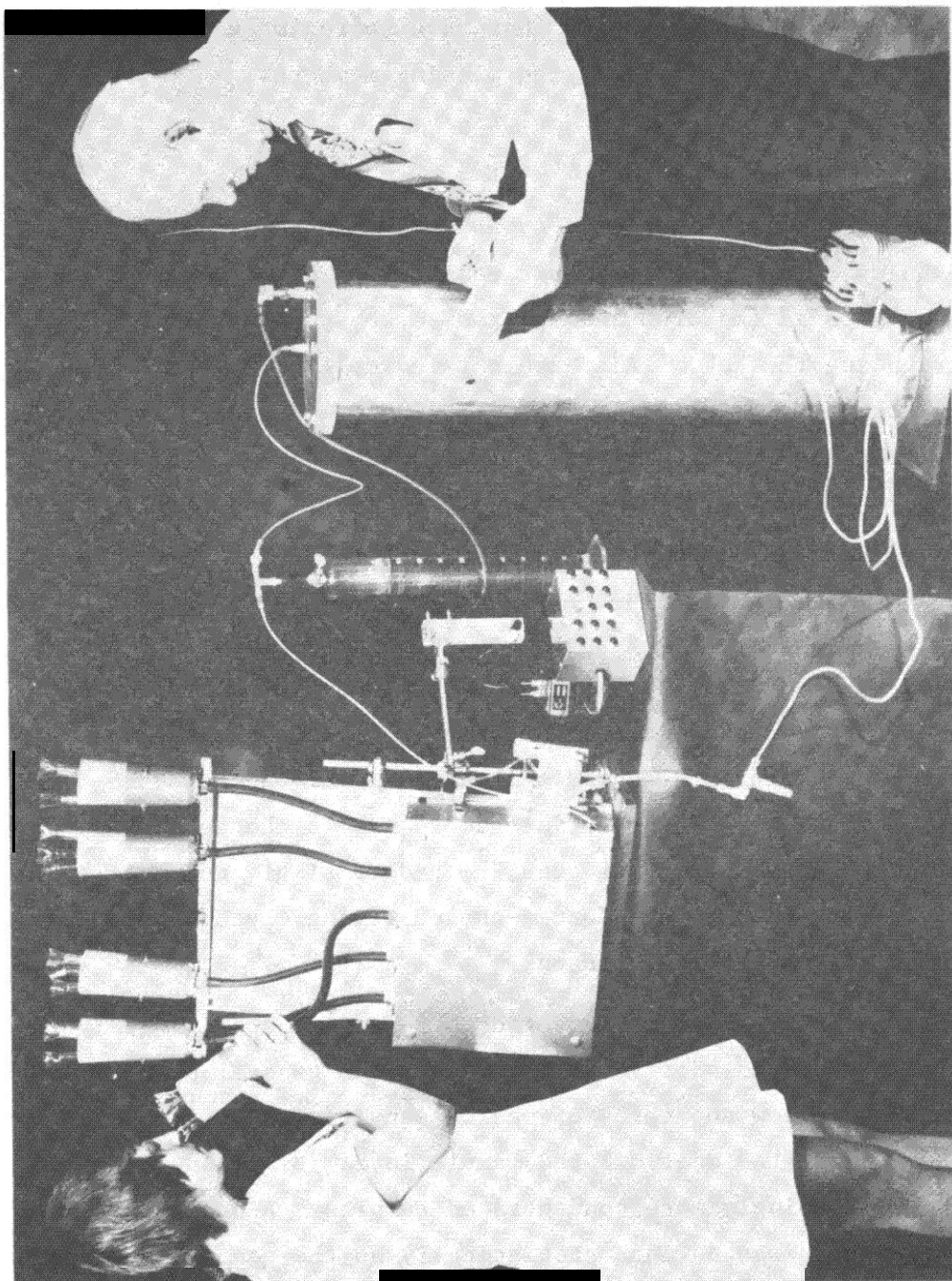


Figure 4. Forced-choice dynamic olfactometer used for evaluation of ambient air sample collected at a dredged material disposal site.

mean of the individual thresholds. It is termed ED₅₀ (Effective Dosage at the 50 percent level) and designates here that extent of dilution at which 50 percent of the panelists would, and 50 percent would not, consistently detect the odor. The ED₅₀ units are numerically equivalent to odor units per cubic foot.

In the forced-choice procedure with nine panelists, one-third, or three panelists, can be correct by chance at an undiluted (higher concentration) level even if all three samples presented at this level are totally nonodorous. Of these three, one-third again, or one panelist, can be again correct by chance at the preceding (3x dilution) level. Such statistical probability would result in a fictitious threshold of 1.4 odor units (Dravnieks, 1976). Values of this kind are not to be taken at face value. Generally, if only three or four of nine panelists are correct at the highest (undiluted) concentration, there is little evidence that the sample is really odorous.

Odor characteristics

The sample bag was disconnected from the olfactometer and was compressed, while still in the aluminum drum, at a rate of 500 ml/min. The bag spout was connected by a Teflon tubing to a glass sniffing port. Panelists smelled the sample exiting from the bag and then completed the descriptor form (Table 1).

The dredged material samples were evaluated as follows. A Tedlar bag was cut at one corner; a 100 to 200-ml mud sample was placed into the bag; and the cut corner was clamped tightly with a special screwclamp. The bag was then inflated with nonodorous air, the sample tossed around in the bag, and the resulting air sample, containing odorous vapors essentially at equilibrium with the dredged material at room temperature, was evaluated for its odor characteristics. A time period of 15 to 30 minutes was allowed for development of an equilibrium concentration of odorous air in the bag. Dredged material treated in the laboratory with various chemicals was sampled

for odors by the same method. Evaluation of odor threshold and odor character of the air in each bag containing treated dredged material proceeded exactly as with the ambient air samples.

In the analysis of the descriptor data, descriptors used by only one panelist in nine were simply noted and recorded in the final data tabulation by a period (e.g., Table 12). Those descriptors used by two or more panelists were further numerically treated. A descriptor may be used at a high score level by a few panelists, or at a low level by many or all. To balance both effects, the following procedure (Dravnieks, O'Donnell, and Reilich, 1975) was used:

- (1) Calculate the percent of panelists who used the particular descriptor for the particular sample.
- (2) Calculate the sum of scores for this descriptor.
- (3) Calculate the sum as the percent of the maximum possible score sum (45 in a group of nine if every panelist gave a score of five).
- (4) Calculate the geometric mean of both of the above percent values. The result is termed the percent applicability of the descriptor.

By this procedure, nine panelists each giving a score of one would produce approximately the same applicability value as five panelists each giving a score of three.

Quantitation and Identification of Bacteria

Quantitation

Weighed samples of dredged material were appropriately diluted and plated upon petri dishes of DSV (*Desulfovibrio*) agar* and BBL MacConkey's agar. DSV agar is an enriched medium containing iron,

*Formula taken from American Type Culture Collection (ATCC), Catalog of Strains; 9th Edition, 1970.

glucose, and yeast extract; it indicates H_2S produced by *Desulfovibrio* species. MacConkey's agar is a selective indicator medium for the presumptive identification of enteric bacteria.

After anaerobic incubation at room temperature (20-25°C bacterial colonies were counted, and the numbers of viable cells per gram wet weight of sample were calculated. The percentage of enteric bacteria was calculated by comparing the number of enteric colonies that grew on MacConkey's agar with the total number of colonies that grew on DSV medium, on a per weight basis of sample. Colonies selected for further study were transferred to agar slants of DSV or Trypticase Soy Maintenance Medium.

Identification

All bacteria were identified and classified according to *Bergey's Manual of Determinative Bacteriology* (Buchanan and Gibbons, 1974). Gram stains were made from colonies selected for identification. Cell morphology, including the identification of spores, was then determined by microscopic examination.

Bacteria presumptively identified as enteric were inoculated into routine diagnostic media for confirmation and final identification. Bacteria presumptively identified as *Bacillus* or *Clostridia* species were inoculated into soil-extract Trypticase Soy Agar for spore studies, into 12% gelatin medium to study gelatin decomposition, and into routine semisolid diagnostic media containing carbohydrates (such as glucose) for further identification as well as for evaluation of gas production. Where warranted, lead-acetate medium was used to detect the production of H_2S by *Clostridia*.

While the identification of methane-producing bacteria, if present, would have been useful, the long time required for their identification exceeded the time-frame of this project. Where possible, all bacteria with the exception of the *Clostridia* were identified

to the species level. *Clostridia* were identified only as to Group (Gp).

Using the above methodology, a number of bacteria were identified including several species of enterics and *Bacillus*, groups of *Clostridia*, and miscellaneous species in other categories.*

Odor Abatement Experiments

Odor abatement experiments were performed with oxidizing agents on subsamples of the dredged material sample from the Detroit, Michigan, disposal area at Grassy Island. Samples from other areas were not used because the initial odor-dilution threshold levels were too low and it would have been difficult to detect any differences in threshold levels between treated and untreated samples.

The reagents used to oxidize odor-producing substances were potassium permanganate (KMnO_4), sodium hypochlorite (NaOCl), hydrogen peroxide (H_2O_2), and ozone (O_3). Simple-aeration and lime [$\text{Ca}(\text{OH})_2$] treatment were also used. The concentrations and contact times were varied. A set of untreated samples was analyzed as well.

For each test of an oxidant, approximately 100 cc of dredged material was placed in a Waring blender. A proper amount of reagent, based on contained solids, was then added to the dredged material and thoroughly mixed for about 1.5 minutes. Ozone was bubbled at 100 ml/min through a sample vigorously shaken in a fritted, glass bubbling flask. The mixture either was put directly into a one-R plastic jar and put aside, or was used immediately, depending upon the contact time required for each test. Samples were transferred to Tedlar

*It is interesting to note that no *Desulfovibrio* organisms were identified. This is not surprising in view of the conclusion (Dunnette, 1973) that such organisms are found principally in the uppermost layers of sediment. Thus, unless the materials sampled represented only the top few centimeters of dredged sediments, dilution would have rendered the isolation of *Desulfovibrio* sp. quite unlikely.

bags prior to testing by an odor panel, as described in a previous section on odor characteristics.

RESULTS

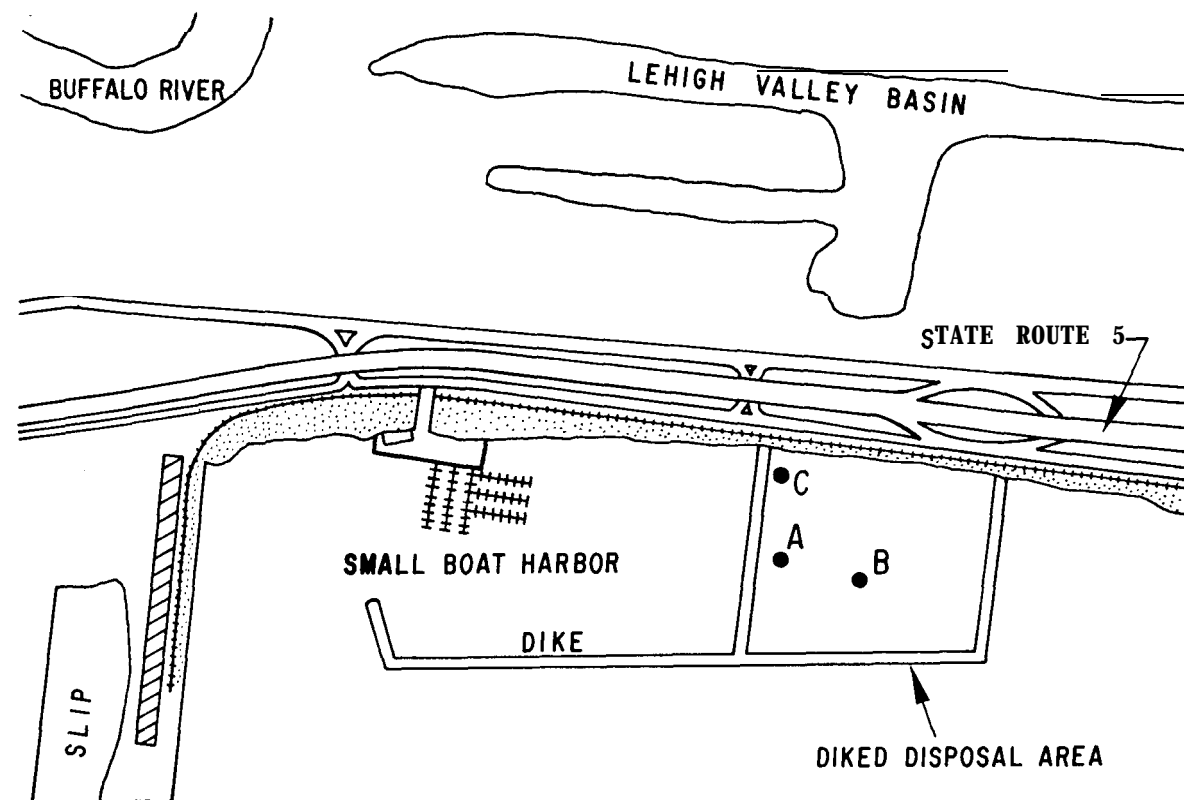
Dredged Material Disposal Sites

Buffalo, New York

This disposal site (Figure 5) is on the south side of Buffalo, on the eastern edge of the outer harbor. The dike encloses a roughly rectangular area measuring approximately 19.5 acres. The disposal site contains material dredged from the Buffalo River Entrance Channel and the Buffalo River proper. Dredged material is customarily transported by Corps hopper dredges to the disposal area. A few small trees and shrubs grow on the surface of the dredged material (Figure 6). A petroleum odor is said to be prevalent during a dredge's six-day work week and an oil slick can usually be seen on water surfaces within the diked area. The odor drops off on Sundays (G. Greener, 1975, oral communication) when dredging and **pumpout** cease. At the time this site was visited, much of the area was above water. The discharge end of the dredge **pumpout** was located near the center of the dredged material area (Figure 5, Point B).

Two visits were made to this site. On July 2, 1975, samples of odorous air were pumped through the Chromosorb samplers, both during material transport while on the hopper dredge LYMAN and at the site (Figure 5, Point A). Unfortunately, two of the samples were improperly analyzed.

On August 7, 1975, samples were taken by all methods; the results of the analyses are presented in Tables 2 to 4. Environmental data were also taken on August 7 and are presented in Table 5. Samples were collected about 48 hours after cessation of pumping by the dredge LYMAN. A faint gasoline or petroleum-like odor was present at the site. According to several workmen, this odor was quite pronounced on the last day the LYMAN operated. Odor-threshold levels, determined from the Tedlar bag samples, are presented in Table 6. The odorogram



BUFFALO OUTER HARBOR

SOUTH BREAKWATER

LAKE ERIE



Figure 5. Map of confined disposal area in Buffalo, NY, outer harbor. Point A indicates where Chromosorb samples, one Tedlar bag, one dredged material sample, and biological samples were taken. Point B indicates downwind site for Tedlar-bag sample, and Point C indicates upwind site for Tedlar-bag sample.

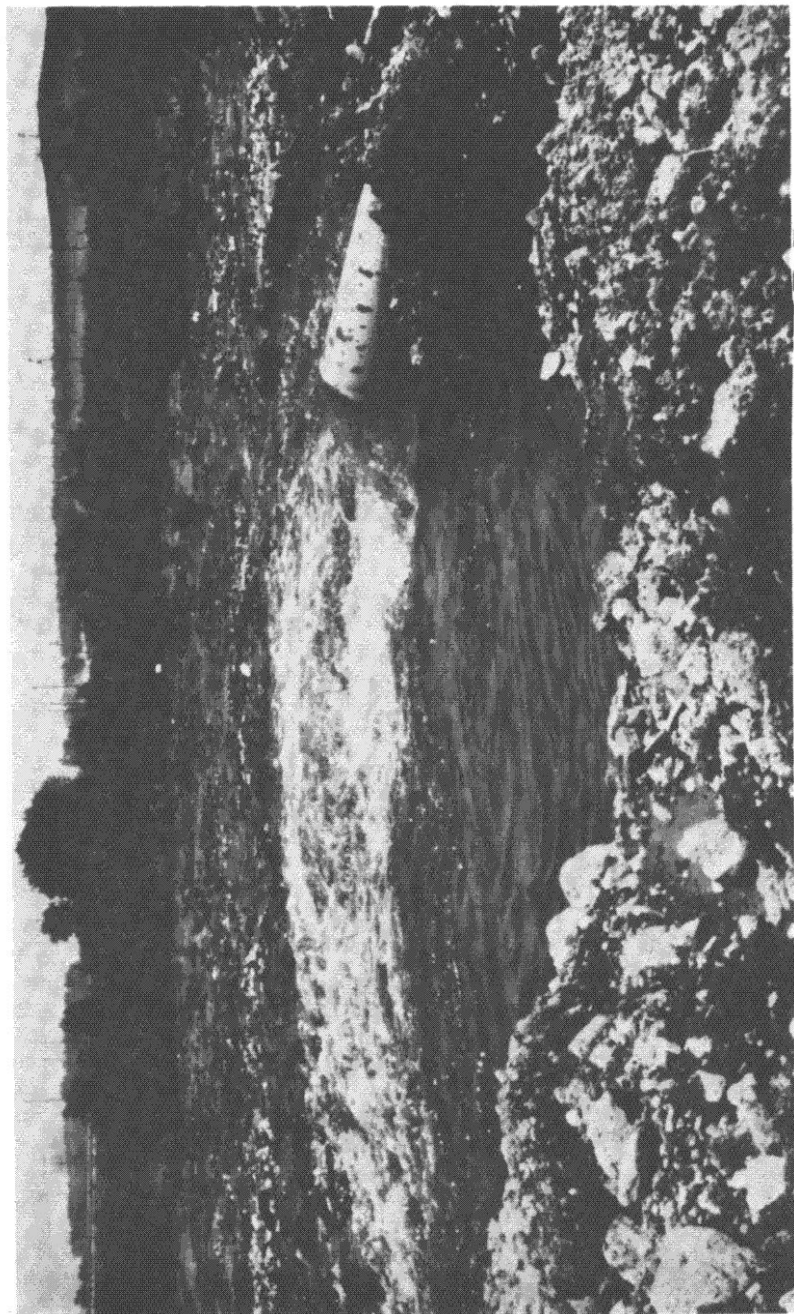


Figure 6. View of pumpout pipe and dredged material in diked disposal area at Buffalo, NY, July 2, 1975.

Table 2

Panelists' Olfactory Sense Evaluation for Dredged
Material Sample Taken at Buffalo, NY

(August 7, 1975; ED₅₀ = 29)

Descriptive Terminology	Descriptor Applicability percent
burnt, smoky	4
sharp, pungent, acid	9
like gasoline, solvent	42
paint-like	4
oily, fatty	24
sickening	31
tar-like	11
burnt rubber	13

Table 3

GC/MS Identified Compounds and Associated Odors
for Chromosorb-collected Sample from Buffalo, NY

(August 7, 1975)

Compounds	GC Peak's Odor Characteristics
acetophenone	no correlation*
1-methylbenzene	"
o-allylphenol	"
mercaptobenzothiazole	"
naphthodioxane	"
terephthaldehyde	"
benzaldehyde	"

*Indicates that although an odorant was found by mass spectrometry, it could not be correlated directly to a specific GC peak on the odorogram obtained from a different instrument.

Table 4

Bacterial Profile of Dredged Material Samples Taken at Buffalo, NY
(August 7, 1975)

Total Cells*		Percent Enterics	Species	H ₂ S	Gas*
DSV**	MacConkey [†]				
2,300,000	10,000	< 1			
			<i>Acinetobacter</i> sp (F)	-	-
			<i>Bacillus coagulans</i> (F)	+	-
			<i>Bacillus circulans</i> , I (F)	-	-
			<i>Bacillus circulans</i> , II (F)	+	-
			<i>Staphylococcus epidermidis</i> (F)	-	-
			<i>Clostridia</i> sp, Gp 2 (A)	+	-

*Colonies per gram wet weight.

***Desulfovibrio* agar medium.

[†]MacConkey's agar medium.

^{††}(F) grows under facultative conditions.

(A) grows under strict anaerobic conditions only.

‡ Produces gas (other than H₂S) in glucose semi-solid medium.

Table 5

Environmental Measurements at Diked DredgedMaterial Disposal Site, Buffalo, NY

(August 7, 1975; 1000 hr CDT)

Variable	Value
Dredged material temperature	18°C
Air temperature	19°C
Relative humidity	75%
Wind speed	< 2 km/hr
Wind direction (from)	45°T
Rainfall, previous two days	.14"
H ₂ S content of air at site	< .007 mg/l
pH of dredged material	7
Odor	petroleum-like

Table 6

Odor-dilution Threshold Levels (ED₅₀)for Samples from Buffalo, NY

(August 7, 1975)

Location*	Sample Type	ED ₅₀
Point A**	Tedlar bag	4.1
Point B	Tedlar bag (downwind)	2.8
Point C	Tedlar bag (upwind)	1.7
Point A	Dredged material	29

*Sampling locations are shown on Figure 5.

**Location of Chromosorb-collected samples.

for the sulfur-specific column indicated the presence of some sulfur compounds, including diethyl sulfide which has an unpleasant odor.

Milwaukee, Wisconsin

This disposal site (Figure 7) is located on the western shore of Lake Michigan in the City of Milwaukee. A dike encloses a submerged fill area of approximately 26.6 acres. This site was being filled (Figure 8) by the hopper dredge HOFFMAN, during the site visit in July, 1975. The odor emanating from the dredged material, while on board the dredge, was sewage-like in nature. Although the odor was not particularly strong, several crew members indicated that the odors sometimes became so noxious that they plugged their noses with cotton. This condition occurred, they said, when the HOFFMAN first began to strip off the upper layer of sediments immediately offshore of the sewage-treatment plant (Figure 7).

On July 15, 1975, samples were taken by all methods; the results of the analyses are presented in Tables 7 to 9. Environmental data were also taken on July 15 and are presented in Table 10. The Chromo-sorb samples were obtained **onboard** the HOFFMAN while it was dredging at Point B (Figure 7). Odor-threshold levels, determined from the Tedlar-bag samples, are presented in Table 11. The odorogram for the sulfur-specific column indicated the presence of sulfur compounds, none of which had odors. (Note that H_2S is not detected by this column.)

Mobile, Alabama

Two disposal sites (Figures 9 and 10), located on the east side of Mobile, were examined. Material at both sites was about three years old at the time of the authors' visit, having been emplaced between September and December of 1972 during a 1,180,000 yd³ maintenance job. Dredged material area No. 1 (Figure 9) is located just north of Routes 16 and 42, on Blakeley Island. Sampling point A

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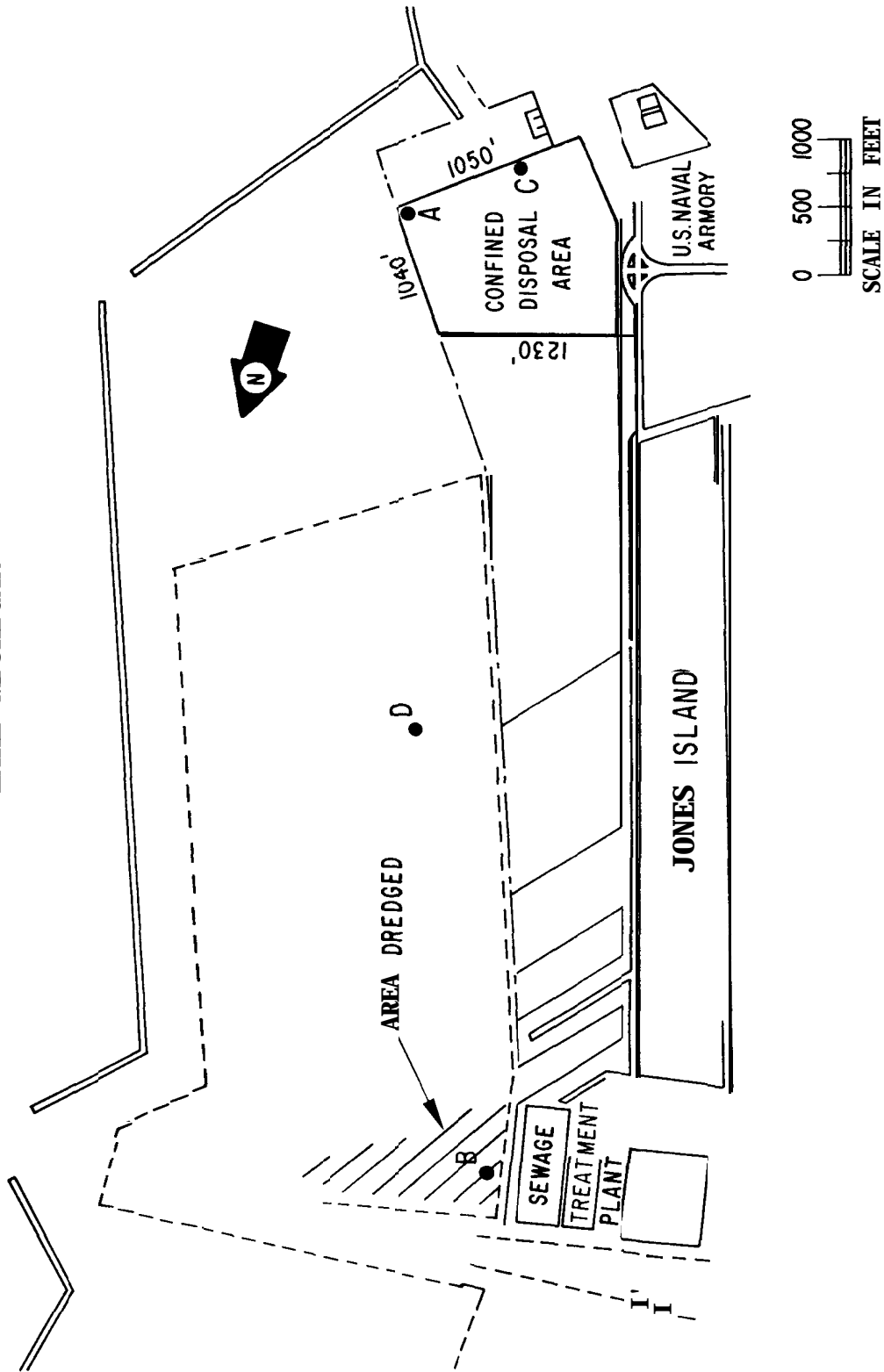


Figure 7. Map of confined disposal area in Milwaukee, WI. Point A indicates where an upwind Tedlar-bag sample was taken, Point B indicates where one Tedlar-bag and one Chromosorb sample were taken, Point C indicates where one Tedlar-bag and the biological sample were taken, and Point D indicates where a Tedlar-bag sample was taken.

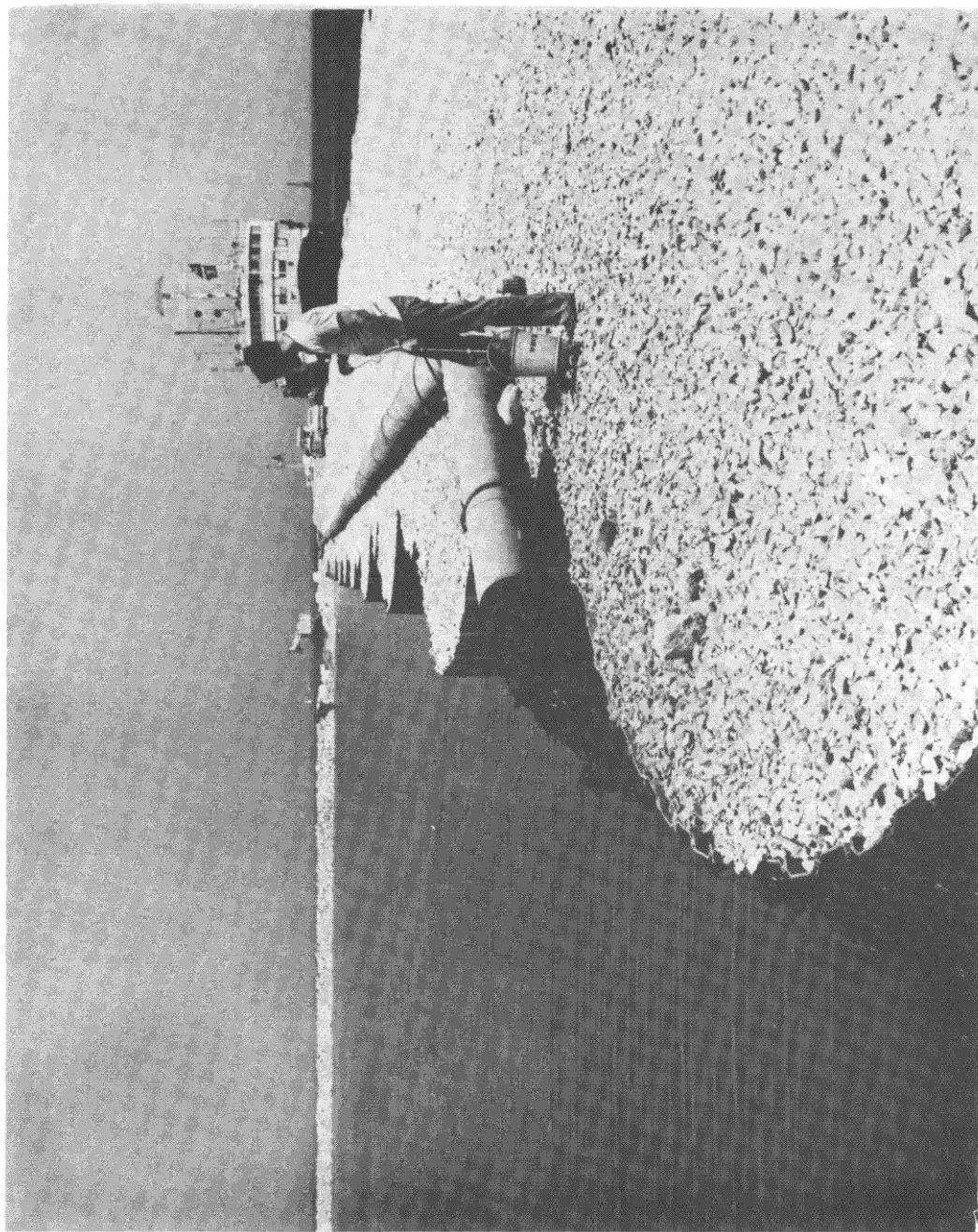


Figure 8. Looking east along south side of Milwaukee, WI, diked dredged material disposal site, hopper dredge HOFFMAN in background, July 15, 1975.

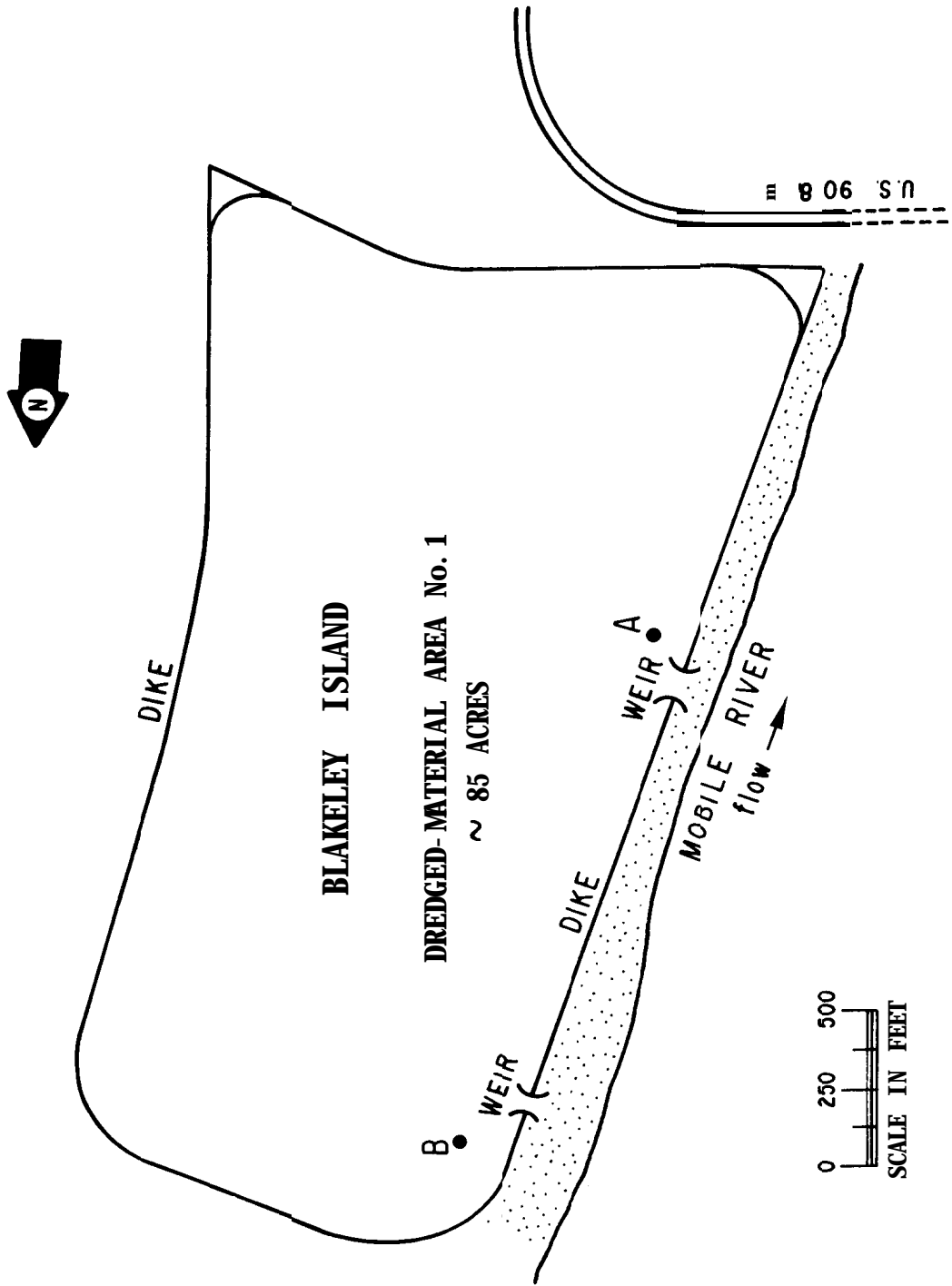


Figure 9. Map of confined disposal area in Mobile, AL (Site I). Point A indicates point where Chromosorb samples, one Tedlar-bag, one dredged material sample, and the biological sample were taken. Point B indicates downwind site for Tedlar-bag sample.

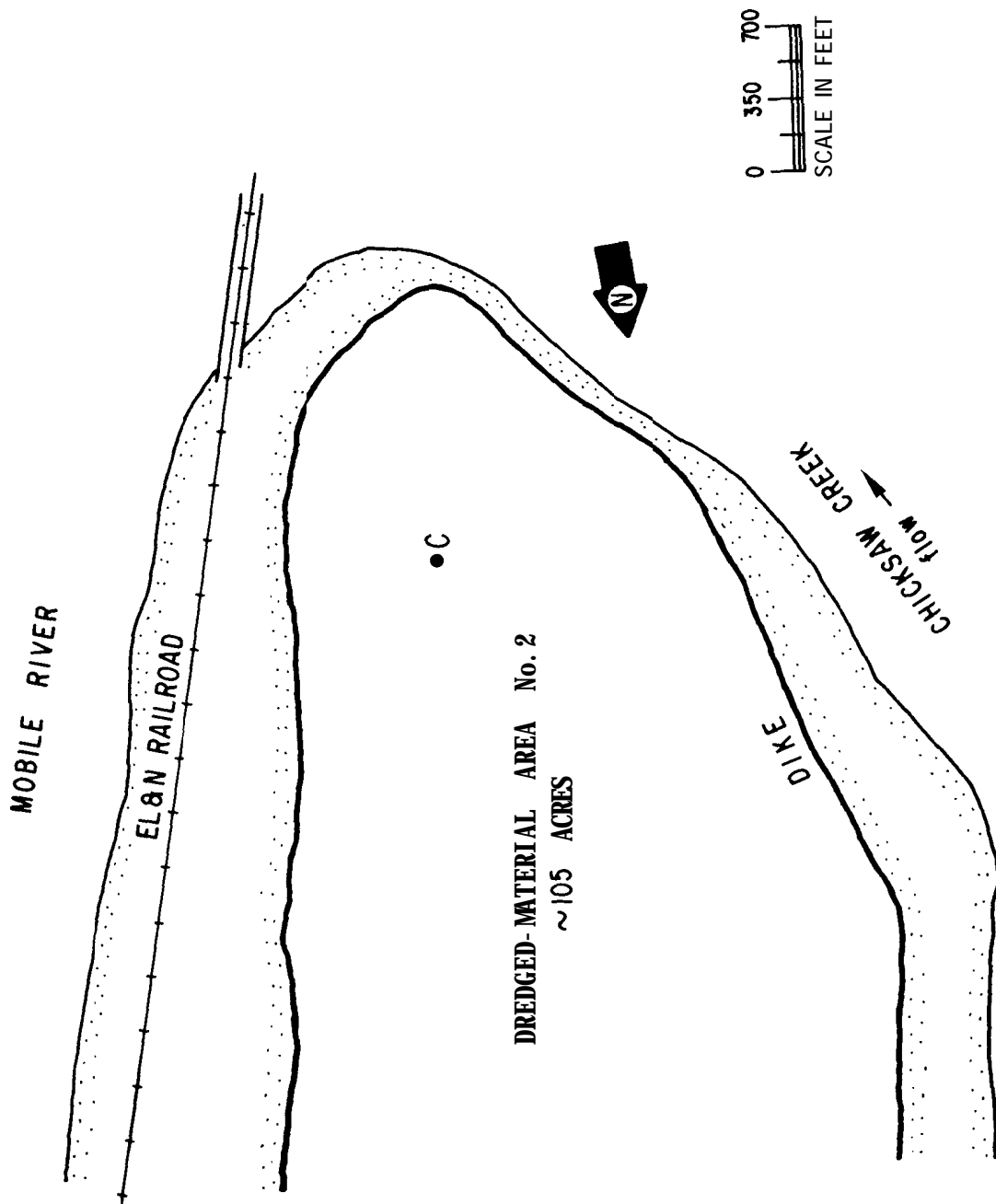


Figure 10. Map of confined disposal area in Mobile, AL (Site II).
Point C indicates where dredged material sample was taken.

Table 7

Panelists' Olfactory Sense Evaluation for
Dredged Material Sample Taken at Milwaukee, WI
 (July 15, 1975)

Descriptive Terminology	Descriptor Applicability percent
burnt, smoky	22
sour, acid, vinegar	18
dry, powdery	7
sharp, pungent, acid	30
putrid	10
sickening	60
tar-like	18
burnt rubber	33
sewer	16
new rubber	11

Table 8

GC/MS-Identified Compounds and Associated Odors
for Chromosorb-collected Sample from Milwaukee, WI
 July 15, 1975)

Compounds	GC Peak's Odor Characteristics
benzaldehyde	unpleasant
heptaldehyde	unpleasant
t-butyl benzene	odor
naphthalene	no odor
3, 5, 5 trimethyl hexanol	no odor
2 ethyl hexanol	no correlation

Table 9

Bacterial Profile of Dredged Material Sample

Taken at Milwaukee, WI

(July 15, 1975)

Total Cells*		Percent Enterics	Species ^{††}	H ₂ S	Gas*
DSV**	MacConkey [†]				
956,000	376,000	39	<i>Alcaligenes fecalis</i> (F)	+	-
			<i>Citrobacter freundii</i> (F)	+	+
			<i>Staphylococcus epidermidis</i> (F)	-	-
			<i>Bacillus circulans</i> (F)	+	-
			<i>Bacteriodes</i> sp (A)	+	-

*Colonies per gram wet weight

***Desulfovibrio* agar medium[†]MacConkey's agar medium^{††}(F) Grows under facultative conditions

(A) Grows under strict anaerobic conditions only

[†]-Produces gas (other than H₂S) in glucose semisolid medium

Table 10

Environmental Measurements on Hopper DredgeHOFFMAN, Milwaukee, WI

(July 15, 1975, 1230 hr CDT)

Variable	Value
Dredged material temperature	16.7°C
Air temperature	31°C
Relative humidity	45%
Wind speed	15 km/hr
Wind direction (from)	225°T
Rainfall, previous two days	negligible
H ₂ S content of air above hopper	< 0.0095 mg/l
pH of material in hopper	8.0
Odor	sewage-like

Table 11

Odor-dilution Threshold Levels for Samplesfrom Milwaukee, WI

(July 15, 1975)

Location*	Sample Type	ED ₅₀
Point A	Tedlar bag (downwind)	1.5 [†]
Point B**	Tedlar bag (dredge pumping)	1.2 [†]
Point C	Tedlar bag (discharge)	18
Point D	Tedlar bag (dredge return trip)	2

*Locations are shown on Figure 7.

**Location of Chromosorb-collected samples.

[†]Value is insignificant; in this low-odor range, an ED₅₀ of 1.2 can result from statistical probabilities alone.

(Figure 9) was inside a recently dug drainage ditch, and the resultant odor intensities may represent the odorosity at the time of dredging. Sample Point B (Figures 9 and 11) would be more representative of odors three years later. Dredged material area No. 2 (Figure 10) is located at the confluence of the Chickasaw Creek and the Mobile River slightly northwest of Site No. 1. Both sites were overgrown with various plants and shrubs, but the growth at Site No. 1 was less than that at No. 2. A marshy and sulfidic odor was observed at Site No. 1, but no odor was observed at Site No. 2.

On July 24, 1975, samples were taken by all methods; the results of the analyses are presented in Tables 12 and 13. Experimental problems presented obtaining GC/MS data. Environmental data were also taken on July 24 at the south and north ends of disposal area No. 1 (Figure 9), and are presented in Tables 14 and 15, respectively. Tedlar-bag samples and dredged material samples were taken at the areas shown in Figures 9 and 10 and the results are presented in Table 16. The odorogram for the sulfur-specific column indicated the presence of some sulfur compounds that were described as "musty."

York Harbor, Maine

This disposal site (Figure 12) is located to the west of York Village on the north side of the York Harbor golf course. The residential area surrounding the site is sparsely populated. The confined disposal area is being filled with dredged material from the York River (Figure 13). The material is transported through the woods via a 12-in.-diameter pipeline about 1/2 mile long.

On August 19, 1975, samples were taken by all methods; the results of the analyses are presented in Tables 17 and 18. The Chromosorb samples showed very low readings and the only compound that could be identified was benzaldehyde. It could not be correlated with any odorogram peaks. Environmental data were also taken

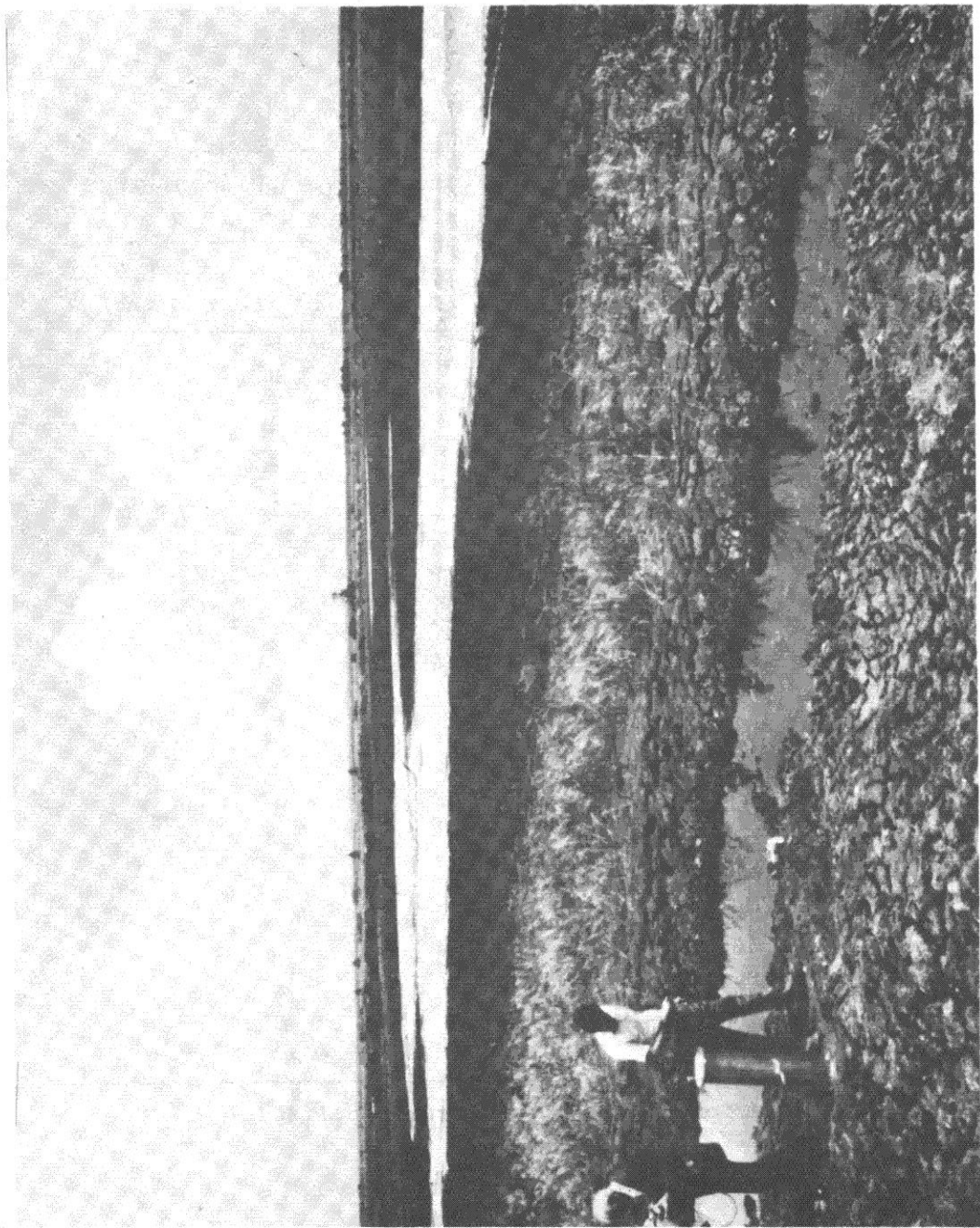


Figure 11. Looking east from top of dike at Blakeley Island, Mobile, AL, diked disposal site, July 24, 1975.

Table 12

Panelists' Olfactory-sense Evaluation for
Dredged Material Sample Taken at Mobile, AL

(July 24, 1975)

Descriptive Terminology	Descriptive Applicability percent	
	Site I (ED ₅₀ = 4.1)	Site II (ED ₅₀ = 8.5)
almond-like	—	22
musk-like	—	13
musty, earthy, moldy	9	18
burnt, smokey	24	31
sour, acid, vinegar	—	•*
oily, fatty	—	7
sharp, pungent, acid	—	•
sweaty	4	25
dry, powdery	9	•
rancid	13	13
animal	•	11
like blood, raw meat	—	16
putrid	4	24
fecal (like manure)	•	•
sickening	24	42
stale	18	18
mushroom	—	22
woody, resinous	•	—
garlic, onion	•	—
metallic	•	—
like mothballs	•	—
like gasoline, solvent	•	—
sewer	16	—
household gas	9	—

*(• means descriptor used by only one panelist).

Table 13

Bacterial Profile of Dredged Material Sample

Taken at Mobile, AL (Site I)

(July 24, 1975)

Total Cells*		Percent Enterics	Species ^{tt}	H ₂ S	Gas [•]
DSV**	MacConkey [†]				
2,040,000	1,650,000	80	<i>Citrobacter freundii</i> (F)	+	+
			<i>Serratia marcescens</i> (F)	—	—
			<i>Proteus mirabilis</i> (F)	+	+
			<i>Brevibacterium</i> sp. (F)	—	—
			<i>Staphylococcus epidermidis</i> (F)	—	—
			<i>Proteus mirabilis</i> (F)	+	+
			<i>Clostridium</i> sp. Gp 3 (A)	—	+

*Colonies per gram wet weight

***Desulfovibrio* agar medium^tMacConkey's agar medium

†† (F) Grows under facultative conditions

(A) Grows under strict anaerobic conditions only

‡ Produces gas (other than H₂S) in glucose semisolid medium

Table 14

Environmental Measurements Made at South End of
Diked Dredged Material Disposal Site I, Mobile, AL

(July 24, 1975; 0900 hr CDT)

Variable	Value
Air temperature	26°C
Relative humidity	97%
Wind speed	5 km/hr
Wind direction (from)	150°T
Rainfall, previous two days	1.0 in.
H ₂ S content of air at site	.31 mg/ℓ
pH of dredged material	7.2
Odor	sulfurous

Table 15

Environmental Measurements Made at North End of Diked
Dredged Material Disposal Site I, Mobile, AL

(July 24, 1975; 1245 hr CDT)

Variable	Value
Air temperature	29°C
Relative humidity	82%
Wind speed	12 km/hr
Wind direction (from)	165°T
Rainfall, previous two days	1.0 inc.
H ₂ S content of air at site	.03 mg/ℓ
Odor	marshy

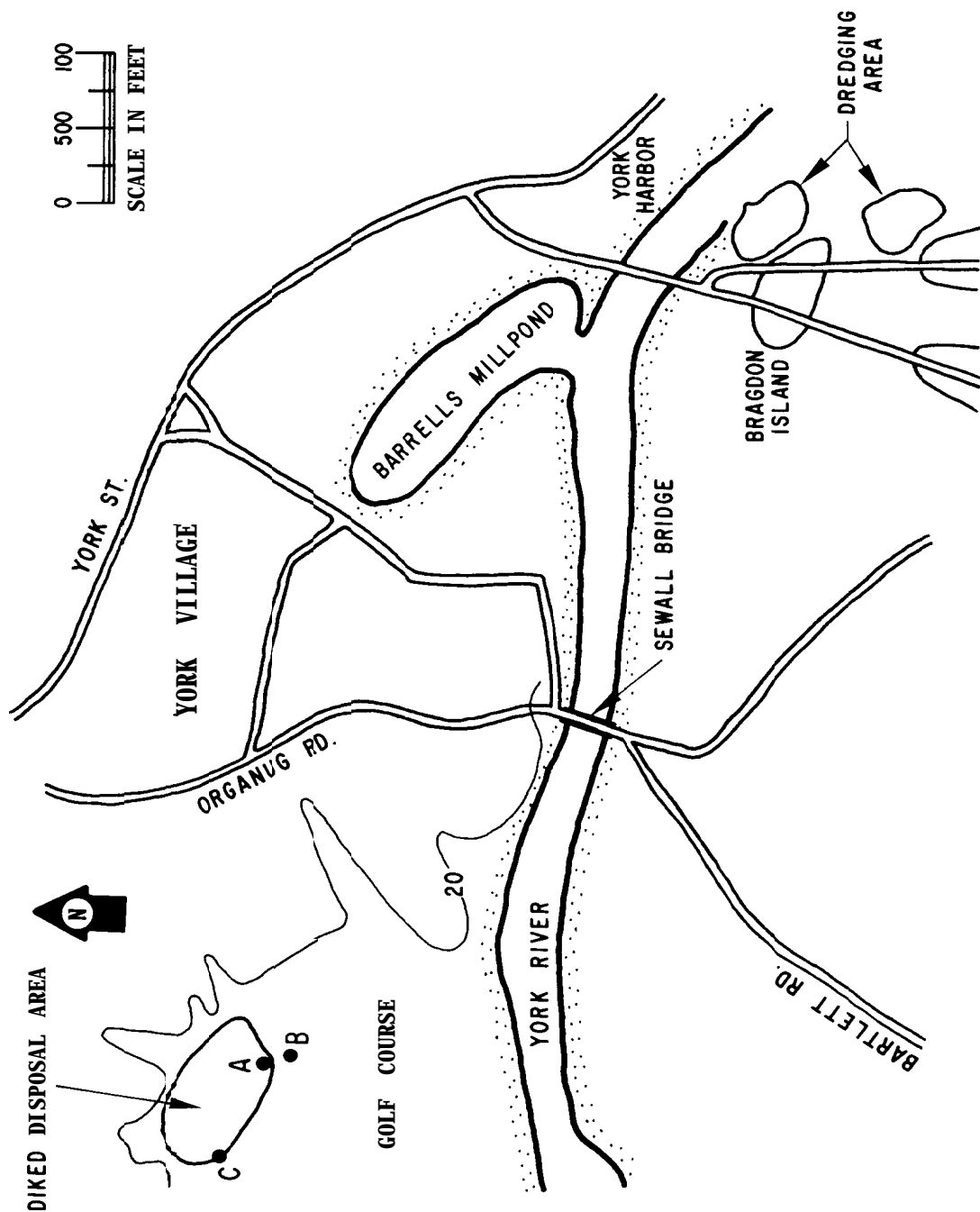


Figure 12. Map of confined disposal area in York Harbor, ME. Point A indicates point where Chromosorb samples, one Tedlar bag, one dredged material sample and a biological sample were taken. Point B indicates downwind site for Tedlar-bag sample, and Point C indicates upwind site for Tedlar-bag sample.

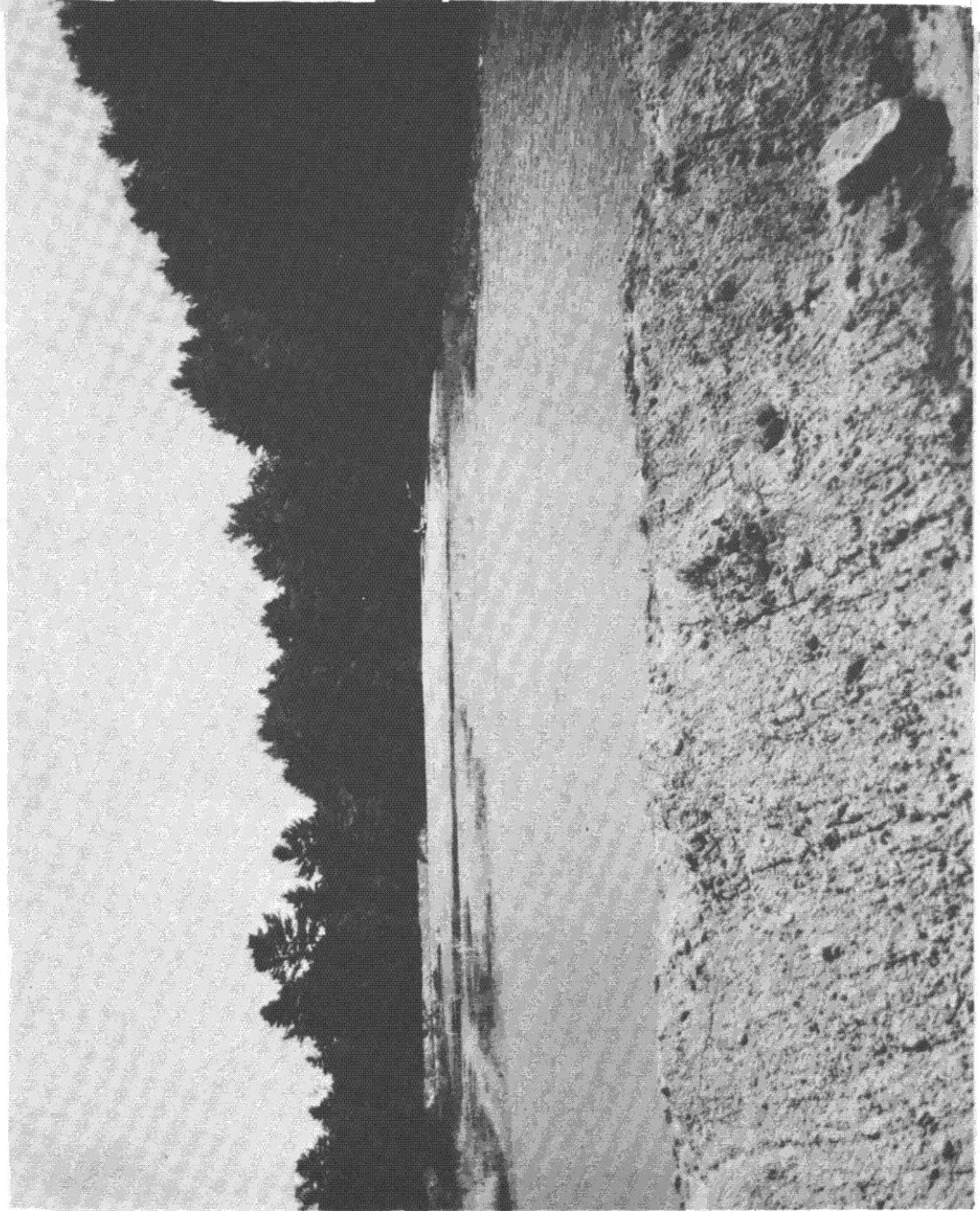


Figure 13. Looking southeasterly across diked, dredged material disposal site at York Harbor ME, August 19, 1975. End of pumpout pipe is at extreme point in background.

Table 16

Odor-dilution Threshold Levels
for Samples from Mobile, AL
 (July 24, 1975)

<u>Location*</u>	<u>Sample Type</u>	<u>ED₅₀</u>
Point A	Tedlar bag	2.2
Point A	Dredged material	4.1
Point B	Tedlar bag (downwind from "A")	2.5
Point c	dredged material	8.5

*Locations are **shown** on Figures 9 and 10

Table 17

Panelists' Olfactory-sense Evaluation for
Dredged Material Sample Taken at
York Harbor, ME
 (August 19, 1975; ED₅₀ = 6.6)

<u>Descriptive Terminology</u>	<u>Descriptor Applicability percent</u>
musty. earthy, moldy	13
burnt, smokey	28
dry, powdery	4
sulfidic	22
putrid	13
sickening	20
household gas	13
paint-like	•*
stale	7
mushroom	.
tar-like	.
sooty	17

*(• means descriptor used by only one panelist)

Table 18

Bacterial Profile of Dredged Material Sample Taken
at York Harbor, ME
 (August 19, 1975)

Total Cells*		Percent Enterics	Species	tt	H ₂ S	Gas ⁺ Gas ⁻
DSV**	MacConkey ⁺					
136,000	5,000	3				
			<i>Proteus mirabilis</i>	(F)	+	+
			<i>Bacillus circulans</i>	(F)	+	-
			<i>Bacillus brevis</i>	(F)	-	-
			<i>Vibrio</i> sp.	(F)	-	-
			<i>Baeteriodes</i> sp.	(A)	+	-

*Colonies per gram wet weight

***Desulfovibrio* agar medium

⁺ MacConkey's agar medium

⁺⁺ (F) Grows under facultative conditions

(A) Grows under strict anaerobic conditions only

[±] Produces gas (other than H₂S) in glucose semi-solid medium

on August 19 and are presented in Table 19. Tedlar-bag samples and a dredged material sample were taken at the points shown on Figure 12. The results of the panelists' determinations are presented in Table 20. The odorogram for the sulfur-specific column indicated that no sulfur compounds were present.

Houston, Texas

This disposal site (Figure 14) is located just north of Galena Park and south of Jacinto City (two suburbs on the northeast side of Houston). The site is known as the Clinton site and covers about 580 acres; it is characterized by many shrubs and willow trees, some more than 15 feet in height (Figure 15). It is being filled by pipeline dredge with material from the upper reaches of the Houston Ship Channel. Dredged material is transported from the Channel to the site via a 15,000-ft, 20-in.-diameter pipe. The dredged material in the discharge area is typically black and oily in appearance, as is the liquid runoff in the immediate area. The solids, after settling, are mostly clean sand containing some red clay and shell fragments.

A malodor counteractant (Custom Industries Counteractant #11) is being used at this site. It is mixed with the dredged material at a ratio of one gallon of counteractant to four gallons of kerosene. The 5-gal solution is then poured directly into the discharge area every two hr. By special arrangement, the counteractant was not added for 48 hr prior to arrival for sample collection.

On August 27, 1975, samples were taken by all methods; the results of the analyses are presented in Tables 21 to 23. Environmental data were also taken on August 27 and are presented in Table 24. Samples were collected at the points indicated on Figure 14. A strong, petroleum-like odor was present at the site. Odor-threshold levels, determined from the Tedlar-bag and dredged material samples, are presented in Table 25. The odorogram for the **sulfur**-specific column indicated that no sulfur compounds were present.

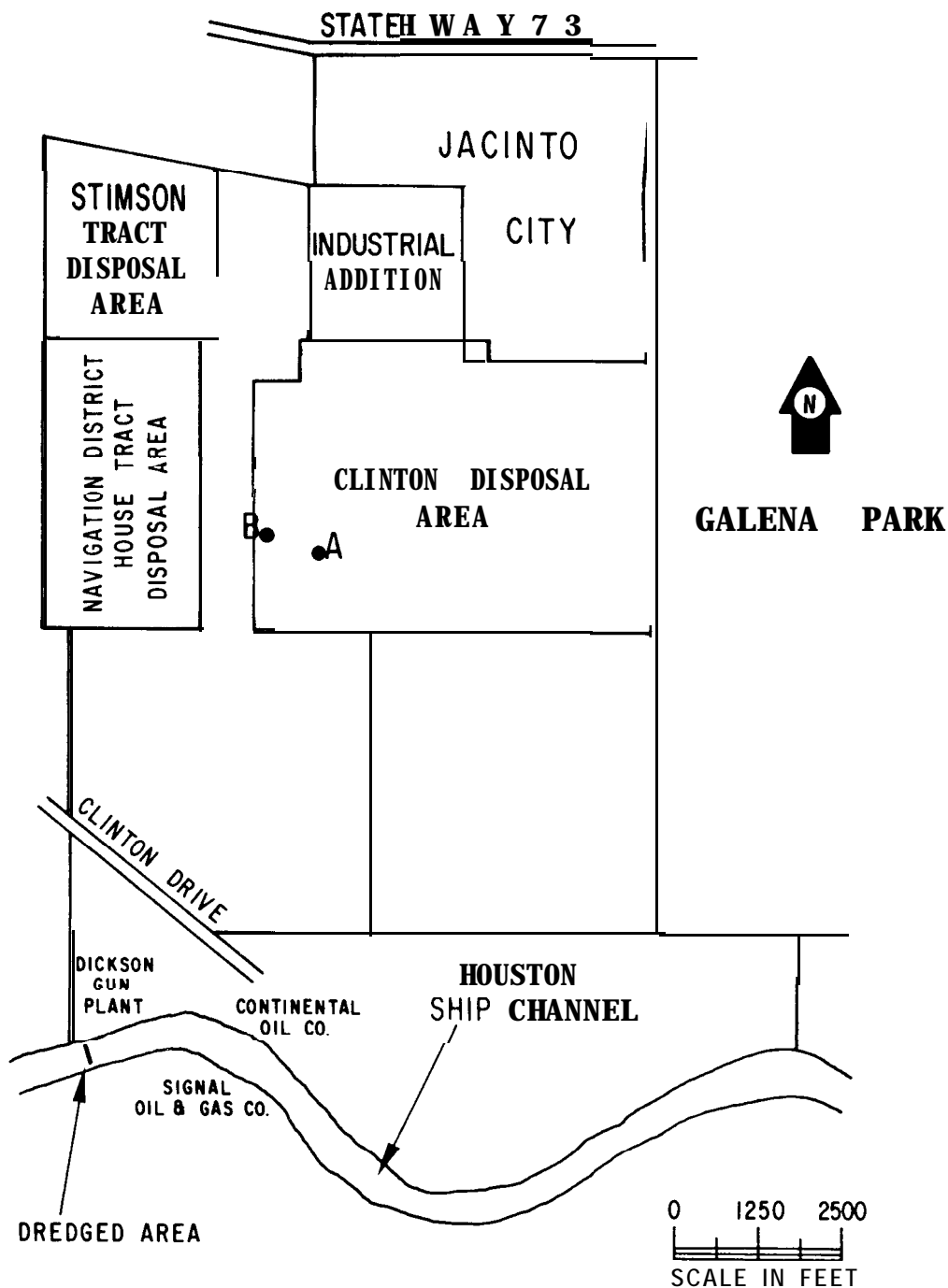


Figure 14. Map of confined disposal area in Houston, TX. Point A indicates where Chromosorb samples, one Tedlar-bag, one dredged material sample and one biological sample were taken. Point B indicates downwind site for Tedlar-bag sample, before and after additive was administered.



Figure 15. End of pumpout pipe at Houston, TX, diked dredged material disposal area on August 27, 1975. Sampling drum for Tedlar-bag samples in foreground.

Table 19

Environmental Measurements made at Diked Dredged
Material Disposal Site, York Harbor, ME
 (August 19, 1975; 1030 hr EDT)

Variable	Value
Dredged material temperature	16°C
Air temperature	20°C
Relative humidity	48%
Wind Speed	Steady breeze
Wind direction (from)	330°T
Rainfall, previous two days	0
H ₂ S content of air at site	.01 mg/ℓ
pH of dredged material	6.5
Odor	muddy

Table 20

Odor-dilution Threshold Levels for Sample from
York Harbor, ME
 (August 19, 1975)

Location*	Sample Type	ED ₅₀
Point A**	Tedlar bag (discharge)	4.6 [†]
Point A	dredged material	1.2 [†]
Point B	Tedlar bag (downwind)	4.1 [†]
Point C	Tedlar bag (upwind)	1.2 [†]

*Locations are shown in Figure 12.

**Location of Chromosorb-collected sample.

[†]Value is insignificant; such a low-odor reading can originate merely from statistical factors.

Table 21

Panelists' Olfactory-sense Evaluation for
Dredged Material Sample Taken at Houston, TX
 (August 27, 1975; $ED_{50} = 10.8$)

Descriptive Terminology	Descriptor Applicability percent
sweet	13
gasoline-like	74
oily, fatty	34
sulfidic	16
sickening	44
household gas	27
kerosene	21
metallic	16
musk-like	10
musty, earthy, moldy	9
burnt, smoky	16
dry, powdery	19
stale	12

Table 22

GC/MS-Identified Compounds and Associated Odors for
Chromosorb-collected Sample from Houston, TX
 (August 27, 1975)

Compounds	GC Peak's Odor Characteristics*
3-isoamylthiophene	no odor
2-n-hexylthiophene	no odor
dimethylfumarate	no correlation
1-methylnaphthalene	no odor
acetophenone	no odor

*Although the individual concentrations of these compounds were too low to exhibit odors, jointly they could produce an odor.

Table 23

Bacterial Profile of Dredged Material Sample

Taken at Houston, TX
(August 27, 1975)

Total Cells*		Percent Enterics	Species ^{tt}	H ₂ S	Gas [‡]
DSV**	MacConkey [†]				
271,000	75,000	27	<i>Staphylococcus epidermidis</i> (F)	—	—
			<i>Pseudomonas</i> sp. (F)	—	—
			<i>Alcaligenes fecalis</i> (F)	—	—
			<i>Citrobacter freundii</i> (F)	+	+
			<i>Bacillus firmis</i> (F)	+	—
			<i>Clostridia</i> sp., Gp 2 (A)	+	+
			<i>Clostridia</i> sp., Gp 3 (A)	+	+

*Colonies per gram wet weight

***Desulfovibrio* agar medium

† MacConkey's agar medium

†† (F) Grows under facultative conditions

(A) Grows under strict anaerobic conditions only

‡ Produces gas (other than H₂S) in glucose semisolid medium

Table 24

Environmental Measurements Made at Diked
Dredged Material Site, Houston, TX

(August 27, 1975; 0930 hr CDT)

Variable	Value
Dredged material temperature	30°C
Air temperature	28°C
Relative humidity	87%
Wind speed	5 km/hr
Wind direction (from)	45°T
Rainfall, previous 2 days	negligible
H ₂ S content of air at site	.6 mg/l
pH of dredged material	6
Odor	petroleum-like

Table 25

Odor-dilution Threshold Levels for
Samples from Houston, TX

(August 27, 1975)

Location*	Sample Type	ED ₅₀
Point A**	Tedlar bag (discharge)	9
Point A	dredged material	10.8
Point B	Tedlar bag (downwind, no counter-actant)	2.5
Point B	Tedlar bag (downwind, counteractant present)	2.5

*Locations are shown on Figure 14.

**Location of Chromosorb-collected samples.

This, on the surface, appears contrary to the GC/MS results (Table 22). The compounds determined by the GC/MS analysis, however, were detected solely by the mass spectrometer. Thus, the MS, being more sensitive than the sulfur-specific column, did detect low concentrations of sulfur compounds.

Detroit (Grassy Island), Michigan

This disposal site (Figure 16) is located on an island in the middle of the Detroit River. The Wyandotte BASF Chemical Company is due west of the site and Fighting Island is due east. The disposal area is about 100 acres in size and the surrounding terrain is grassy with some weeds about 4 to 5 ft high. During the site visit, dredged material was being transported from the Rouge River to the dredged material disposal site area by a hopper dredge. The flow from the dredge to the disposal site was accomplished by two pipes: one pipe to the main disposal area (Figure 16), the other to the four small basins (Figure 16, Point A) where various sedimentation and plant-growing experiments were being conducted.

On September 23, 1975, samples were taken by all methods; the results of the analyses are presented in Tables 26 to 28. Environmental data were also taken on September 23 and are presented in Table 29. Samples were collected at the points noted on Figure 16. A gasoline-like odor was present at the site. The odor, however, decreased markedly after cessation of the pumping operation. The odor threshold levels are presented in Table 30. An odorogram for the sulfur-specific column indicated the presence of 15 sulfur compounds. One of these, diethyl sulfide, had a particularly unpleasant odor.

Anacortes, Washington

This disposal site (Figure 17) encloses a roughly rectangular area measuring approximately 200 acres in size. At the time of the

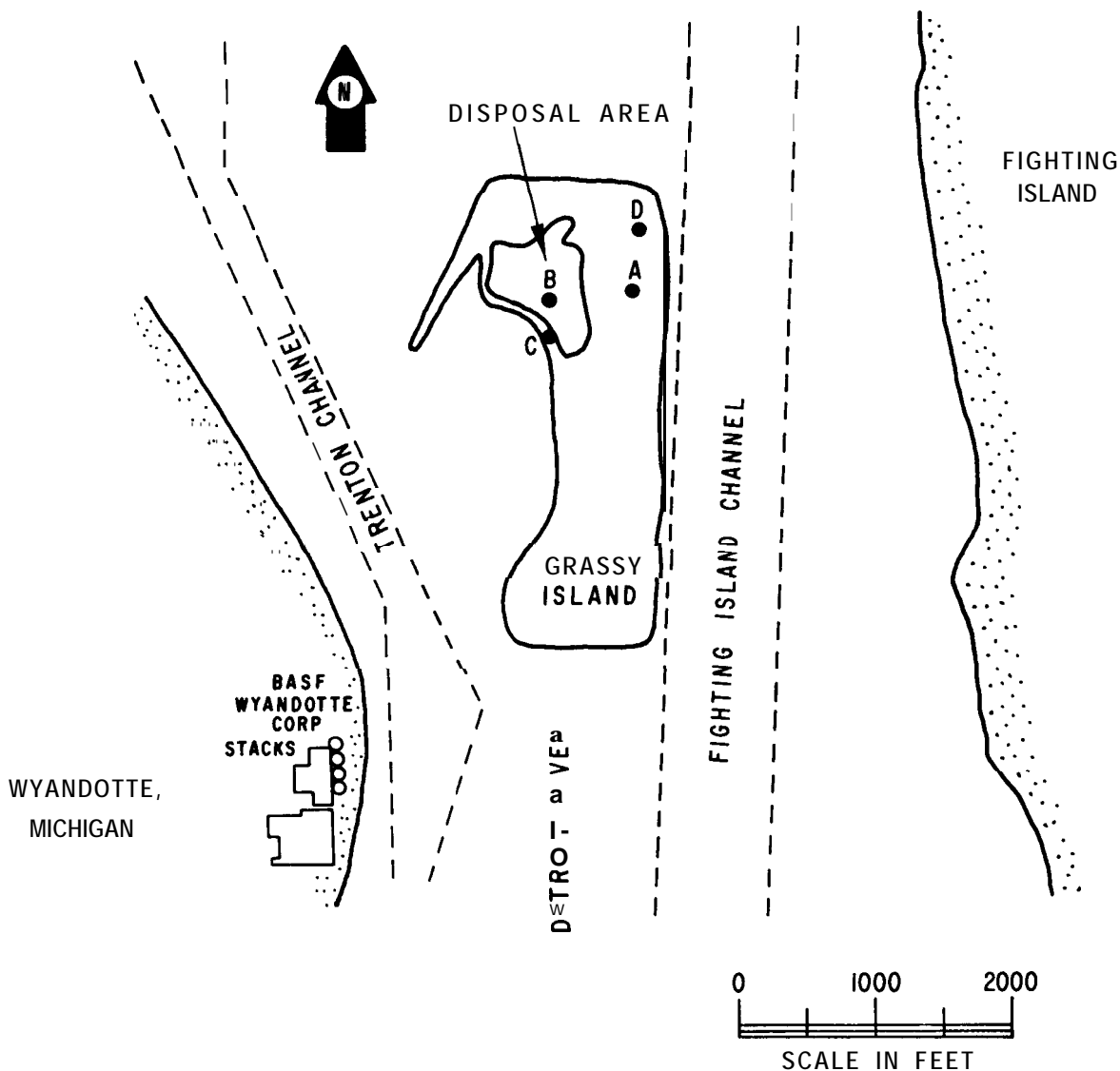


Figure 16. Map of confined disposal area near Detroit (Grassy Island), MI. Point A indicates where Chromosorb samples were taken. Point B indicates where a Tedlar bag, dredged material samples, and biological samples were taken. Point C indicates downwind site for Tedlar-bag sample. Point D indicates upwind site for Tedlar-bag sample.

Table 26

Panelists' Olfactory-sense Evaluation for Dredged
Material Sample Taken at Detroit (Grassy Island), MI
 (September 23, 1975; ED₅₀ = 46)

Descriptive Terminology	Descriptor Applicability percent
sweaty	17
burnt, smoky	32
sour, acid, vinegar	17
sickening	45
tar-like	27
medicinal	•*
kerosene	16
sooty	.
gasoline-like	71
rancid	9
aromatic	9
cleaning fluid	27
woody, resinous	16
metallic	14
sharp, pungent, acid	31
oily, fatty	28
stale	.
sewer	
new rubber	16
burnt rubber	16

* (• means descriptor used by only one panelist)

Table 27

GC/MS-identified Compounds and Associated
Odors for Chromosorb-collected Sample From
Detroit (Grassy Island), MI
 (September 23, 1975)

Compounds	GC Peak's Odor Characteristics
naphthalene	odor
ethylbenzaldehyde	no odor
ethylbenzene	odor
benzaldehyde	no correlation
1-methyl indan	unpleasant
o-ethyl toluene	no correlation
1-chlorooctane	burnt
cyclooctatetraene	no odor
isopropenyl hexene	unpleasant

Table 28

Bacterial Profile of Dredged Material Sample

Taken at Detroit (Grassy Island), MI

(September 23, 1975)

Total Cells*		Percent Enterics	Speciestt	H ₂ S	Gas [‡]
DSV**	MacConkey†				
300,000	66,000	22	<i>Alcaligenes fecalis</i> (F)	+	—
			<i>Citrobacter freundii</i> (F)	+	+
			<i>Bacillus firmis</i> (F)	+	—
			<i>Bacillus lentus</i> (F)	+	—
			<i>Staphylococcus epidermidis</i> (F)	—	—

*Colonies per gram wet weight

***Desulfovibrio* agar medium

^tMacConkey's agar medium

^{††} (F) Grows under facultative conditions

(A) Grows under strict anaerobic conditions only

[‡] Produces gas (other than H₂S) in glucose semisolid medium

Table 29

Environmental Measurements Made at Diked
Dredged Material Disposal Site, Detroit
(Grassy Island), MI

(September 23, 1975; 1545 hr EDT)

Variable	Value
Dredged material temperature	19°C
Air temperature	17°C
Relative humidity	64%
Wind Speed	14 km/hr
Wind direction (from)	57°T
Rainfall, previous 2 days	negligible
H ₂ S content of air at site	< .002 mg/l
pH of dredged material	7.5
Odor	petroleum-like

Table 30

Odor-dilution Threshold Levels for Samples
from Detroit (Grassy Island), MI

(September 23, 1975)

Location*	Sample Type	ED ₅₀
Point B**	Tedlar bag (discharge)	18
Point B	dredged material	46
Point C	Tedlar bag (downwind)	4.1 [†]
Point D	Tedlar bag (upwind)	1.1 [†]

*Locations are shown on Figure 16.

**Location of Chromosorb collected samples.

[†]Value is insignificant.

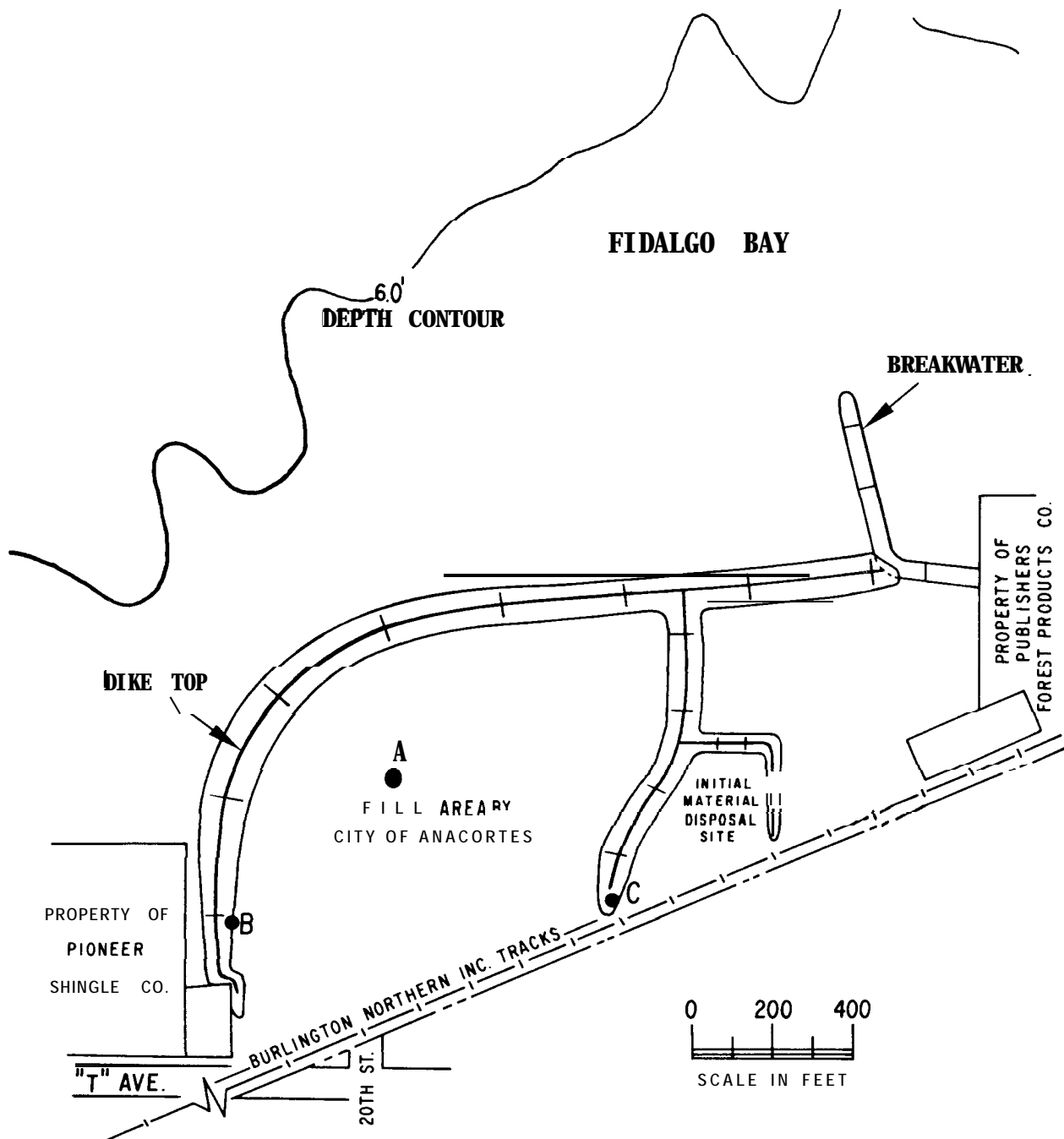


Figure 17. Map of confined disposal area in Anacortes, WA. Point A indicates where Chromosorb samples and one Tedlar-bag sample were taken. Point B indicates where a downwind Tedlar bag and a dredged material sample were taken. Point C indicates where a Tedlar-bag sample was taken.

site visit, all but a few acres (Figure 18) surrounding Point A (Figure 17) were underwater. The disposal site was being filled by pipeline dredge with material from Station 1500 in Fidalgo Bay, at the bend in the navigation channel. According to a Corps Inspector at the site, malodors had not been a problem at the site during the most recent disposal operation. He had noticed weak "sulfurous" or "fishy" odors on occasions after pumping had ceased for about a day and water had drained off the pile of dredged material. The authors could not detect odors at the end of the discharge pipe (Figure 17, Point A) when the dredge was cutting deep below the sediment surface. When the cutter head was operating in the organic-rich, near-surface sediments, however, a "sulfidic" malodor was detected. Although the area around the site is industrialized, the authors did not detect any significant competing malodors on the day they sampled.

On October 1, 1975, samples were taken by all methods; the results of the analyses are presented in Tables 31-33. Environmental data were also taken on October 1, and are presented in Table 34. Samples were collected at the points noted on Figure 16. Odor threshold levels, determined from Tedlar bag and dredged material samples, are presented in Table 35. The odorogram for the sulfur-specific column did not indicate presence of sulfur compounds.

Odor Abatement Experiments

Table 36 gives the results of the odor-abatement experiments in terms of odor-dilution threshold levels (ED_{50}) for oxidant-treated subsamples of the Grassy Island dredged material sample. Included also are evaluations for three untreated subsamples. Experimental results (Table 36) are in chronological order; evaluation of an untreated sample begins each sequence of evaluations made on each of three consecutive days of experiments. Table 37 presents the results in a pooled form, by treatments. Standard deviations of $\log ED_{50}$ are also given, to facilitate analysis of the data.

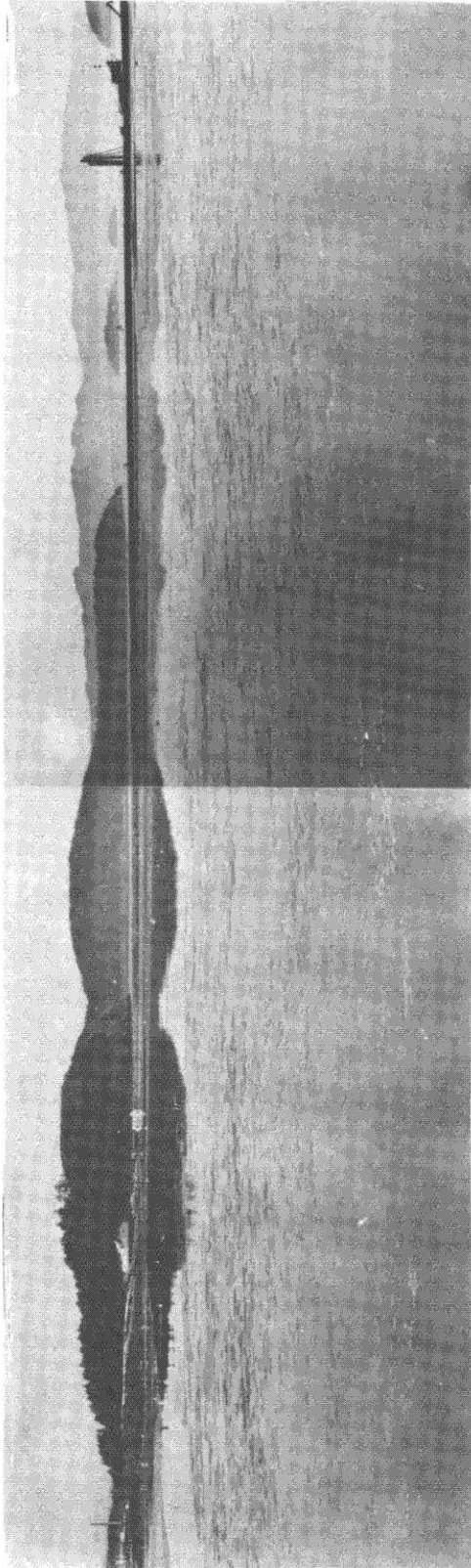


Figure 18. View to north across diked dredged material disposal site at Anacortes, WA, October 1, 1975.

Table 31

Panelists' Olfactory-sense Evaluation for
Dredged Material Sample Taken at Anacortes, WA
 (October 1, 1975; ED₅₀ = 2)

Descriptive Terminology	Descriptor Applicability percent
sweet, smoky	12
dry, powdery	10
disinfectant	15
sweet	12
etherish	•
musty, earthy, moldy	•
like gasoline, solvent	•
oily, fatty	•
rancid	•
sickening	•
cleaning fluid	•
sooty	•

*(• means descriptor used by only one panelist)

Table 32

GC/MS-identified Compounds and Associated
Odors for Chromosorb-collected Sample from
Anacortes, WA

(October 1, 1975)

Compounds	GC Peak's Odor Characteristics
ethyl benzene	no odor
allylbenzene	no correlation
o-ethyl toluene	no correlation
isopropenyl benzene	faint
1-methyl indan	very unpleasant
benzaldehyde	no odor
acetophenone	no odor
dimethyl acetophenone	no correlation
diethyl phthalate	no correlation
terephthaldehyde	no correlation
naphthalene	no correlation
p-xylene	no odor

Table 33

Bacterial Profile of Dredged MaterialSample Taken at Anacortes, WA

(October 1, 1975)

Total Cells*		Percent Enterics	Species ^{††}	H ₂ S	Gas [‡]
DSV**	MacConkey†				
< 2000	30,000	--	<i>Alcaligenes fecalis</i> (F)	--	--
			<i>Proteus mirabilis</i> (F)	+	+
			<i>Bacillus coagulans</i> (F)	+	--
			<i>Staphylococcus epidermidis</i> (F)	--	--
			<i>Bacillus sphaericus</i> (F)	+	--

*Colonies per gram wet weight

***Desulfovibrio* agar medium[†]MacConkey's agar medium^{††}(F) Grows under facultative conditions

(A) Grows under strict anaerobic conditions only

[‡]Produces gas (other than H₂S) in glucose semisolid medium

Table 34

Environmental Measurements Made at Diked
Dredged Material Disposal Site, Anacortes, WA
 (October 1, 1975; 0805 hr PDT)

Variable	Value
Dredged material temperature	22°C
Air temperature	14°C
Relative humidity	dry
Wind speed	calm
Wind direction	calm
Rainfall, previous 2 days	none
H ₂ S content of air at site	.035 mg/l
pH of dredged material	6.8
Odor	slightly sulfurous

Table 35

Odor-dilution Threshold Levels for Samples
from Anacortes, WA
 (October 1, 1975)

Location*	Sample Type	ED ₅₀
Point A**	Tedlar bag (discharge)	4.6
Point B	Tedlar bag (downwind)	3.6
Point B	Dredged material	2
Point C	Tedlar bag (downwind, at weir intake)	5.9

*Locations are shown on Figure 17.

**Location of Chromosorb-collected samples.

Table 36

ED₅₀ Values for Untreated and Oxidant-Treated Subsamples of
Detroit (Grassy Island), MI, Dredged Material Sample

Treatment	ED ₅₀ Values After Contact Times Indicated in Hours								
	<u>0</u>	0.08	0.5	1	1.5	<u>2</u>	17	22	24
None	68								
KMnO ₄ 1%			5					23	
" 2%			40	15					
" 2.5%			22	37		37	10		
" 4%							33		
None	125								
NaOCl 1%			78	53			37		
" 1.5%			98		47		11		
" 2%							101		
Ozone 1 ppm		98							
" 5 ppm		110							
" 10 ppm		110							
Aeration					125				29
None	37								
H ₂ O ₂ 1%			8			32			
" 2%			29	60		16			
Ca(OH) ₂ 0.6%						33			
" 0.7%			47			14			

Table 37

Analysis of ED₅₀ Data from Table 36

Treatment	Number of Data Points	Mean Log ED ₅₀		Mean ED ₅₀	Percent ED ₅₀ Units Compared with Non-Treated
		Value	Standard Deviation		
None	3	1.83	0.26	68	100
KMnO ₄	9	1.32	0.31	21	30
NaOCl	7	1.70	0.33	50	74
Ozone	3	2.02	0.03	160	156
Aeration	2	1.73	0.45	60	84
H ₂ O ₂	5	1.37	0.33	23	35
Ca(OH) ₂	3	1.45	0.27	28	41

The standard deviation for untreated samples is 0.26. This is higher than the 0.1 value usually obtained in repeated measurements of ED_{50} for samples of constant concentration, using experienced odor panels of nine members (Dravnieks, Prokop, and Boehme, 1975). The most likely explanation for the difference is the variability in odorant concentration in the subsamples due to the non-homogeneity of the master dredged material sample. The master sample contained 20 percent solids and was difficult to homogenize while taking subsamples.

An increase in the concentration of an oxidant did not increase its efficiency of odor abatement (Table 36). Likewise, an increase in contact time did not produce better odor abatement. The pooled data in Table 37 indicate, however, that all treatments, except the short ozonization, produced a decrease in odor. The probable explanation is that a relatively small amount of oxidant is sufficient to oxidize the most odorous components; addition of more oxidant, or an extension in the contact time, does not affect the concentration of the more stable oxidants.

This relative independency on the concentration and contact-time permit comparison of data by pooling the values by treatments. The last column in Table 37 indicates that if the mean ED_{50} for all untreated samples is taken to represent 100 percent odor, two types of treatments, $KMnO_4$ and H_2O_2 , produced an approximately threefold decrease in the odor level, and $NaOCl$ decreased it, but by only 26 percent. The number of data points for the aeration and lime treatments is too small to draw definite conclusions.

The statistical significance of the data from the abatement experiments was assessed by the Wilcoxon Rank Sum Test (Beyer, 1968). As applied here, data for samples treated by a chemical and for non-treated samples are arranged in order of descending magnitude, and ranked jointly with the untreated samples represented by values in parentheses, and Roman numerals showing ranks by magnitude:

KMnO₄ Treatment

(125), (68), 40, 37, (37), 37, 33, 22, 15, 10, 5

I II IV v VI

H₂O₂ Treatment

(125), (68), 60, (37), 32, 29, 16, 8

I II IV

The rank sum for the untreated group is 8 for the KMnO₄ series, and 7 for the H₂O₂ series. Tables for the Wilcoxon test indicate that the KMnO₄ effect exists at $p = 0.05$ (the 95 percent confidence level), and the H₂O₂ effect at $p = 0.10$ (the 90 percent confidence level). Thus, both effects seem to be real.

The effect of NaOCl was statistically insignificant when analyzed by the Wilcoxon test. However, it may be that in this case a particularly odorous set of subsamples, with an untreated sample at $ED_{50} = 125$, was treated. The data (Table 36) on the ozonized and the first aerated sample, all obtained on subsamples of the same day, support this assumption.

The standard logarithmic deviation for the seven NaOCl-treated samples (Table 37) is 0.33, and the logarithmic mean ED_{50} is 1.70. The $\log ED_{50}$ for the untreated sample of the same day is 2.10 (= $\log 125$). The extent of deviation of this untreated sample from the NaOCl-treated group is measured in terms of a statistical z-coefficient, calculated as follows (cf. Langley, 1970)

$$z = \frac{\sqrt{7}(2.10-1.70)}{0.33} = 3.2$$

where the values are defined in the text above; 7 represents the number of samples in the treated group. Such a deviation is significant at $p < 0.01$ (more than the 99 percent confidence level),

and the odor abatement to 50/125 (40% of the initial value) might have resulted from the NaOCl treatment.

The limited number of oxidation experiments indicate that KMnO_4 , H_2O_2 , and possibly NaOCl can reduce odor by a factor of 2 to 3.

Odor character of the dredged material samples was modified by the oxidation treatments only to a very limited extent. A kerosene-like odor note was consistently removed by the KMnO_4 treatment, and putrid and rancid odor notes subsided after overnight contact time. Treatment with NaOCl effected a somewhat less-consistent reduction in the kerosene-like odor note, and tended to generate a sweet odor note. Ozone treatment also tended to introduce a sweetish note.

In both ozonization and aeration, the contact between the gas phase and the dredged material subsamples was rather poor because of the density of the slurry, and despite vigorous agitation of the samples.

DISCUSSION

Degree of Odor Problem

Seven site visits and odor measurements on samples from those sites cannot fully reflect the range of odor problems at dredged material disposal sites. Nevertheless, the data from these sites represent all known locations where odor problems were reported at Corps of Engineers' diked disposal sites during the summer months of 1975.

Direct observations during site visits did not reveal any cases of severe odor problems. Odors at most sites were generally detectable but were not overpowering even in close vicinity to the most odorous of dredged material discharges.

Measurements of the odor-unit contents of collected samples (Tables 6, 11, 16, 20, 25, 30, and 35) can be interpreted by reference to various typical odor-control regulations. Odor-character data (Tables 7, 12, 17, 21, 26, and 31) can be analyzed in terms of odor genesis and possible practical consequences.

Magnitude of odor emissions

In odor-control technology, it has been customary to measure odor emission by two related parameters:

- (1) odor-unit content: volume dilution needed to reduce one volume of odorous sample to threshold and traditionally stated in x odor units per cu ft,
- (2) total odor emission, which is the number of odor units per cu ft multiplied by the volumetric emission rate (cu ft/min). Thus, 1000 cu ft per min of an emission with a 12 odor unit per cu ft corresponds to $12 \times 1000 = 12,000$ odor units/min total odor emission.

There are no federal regulations on odor emission, but many states and local authorities indicate odor levels at which, on the basis of their limited experiences, odor nuisances might be **expected** (Leonardos, 1974).

Thus, Minnesota's regulation (State of Minnesota, 1971) prohibits an odor emission in excess of 25 odor units from sources less than 50 ft above grade elevation, and prohibits a total odor emission rate over 1,000,000 odor units per minute per source. A proposed San Francisco Bay Area (SFBA) regulation, for sources less than 30 ft above grade, prohibits emissions if they remain odorous after 1000-fold dilution with odor-free air. Furthermore, the SFBA regulation proposes that resulting ambient odors at the property line bounding the odor source should be capable of control by not more than a fourfold dilution with odorless air.

An inspection of the odor unit tables indicates that none of the emissions from actual dredged material sources (at discharge) approached the above-stated, odor-unit content. Only the air sample in equilibrium with dredged material sampled at Grassy Island, MI (46 o.u.), and Buffalo (29 o.u.), would not satisfy the stringent Minnesota regulation. This, however, would correspond to a hypothetical case in which a large mass of dredged material were continuously and effectively stripped of odorous substances by a relatively small flow of air, and certainly would not apply to a resting surface.

Air samples taken on dikes downwind from the dredged-material odor sources did not exceed the specifications of the SFBA regulation.

Total odorous emission is easily estimated for sources such as stacks where total volumetric flow is known. In the dredged material disposal situation, however, only crude estimates are possible. As an example of such an estimate, assume that the end of a pumpout pipe

discharging dredged material with much splashing is 2 to 3 ft above the disposal area surface. In some observations, such a discharge appears to result in a cloud of droplets surrounding the end of the discharge pipe. Assume now that the cloud is semi-spherical, with a radius of 10 ft, and uniform in its odor content; e.g., 18 o.u./cu ft (Grassy Island and Milwaukee cases) throughout this volume. Assume further that a wind of 5 mph moves air through such a steady-state cloud so that the air emerges perfectly saturated with an odor concentration of 18 o.u./ft³. In this case, the semisphere has a cross section of 157 sq ft and the emission rate is $\frac{5 \times 5280 \times 157 \times 18}{60}$ = 1,243,440 odor units per min in total, only 24% above the Minnesota maximum of 1,000,000 odor units. These assumptions are all in favor of producing a high estimate of total odor-unit emission; the actual total emission should be considerably less. Higher wind speeds may result in lesser equilibration and the cooling of droplets by evaporation would reduce their odorosity.

The surface of the dredged material in the diked area may constitute another type of odor source. Air above the surface accepts odorous vapors, but it is very doubtful if odor contents of Tables 6, 11, 16, 20, 25, 30, and 35, for air equilibrated with the dredged material would apply to the boundary film of air at a surface of resting dredged material. Diffusion of odorants through dredged material to the surface is probably the rate-limiting step here and, in reality, the surface of the dredged material would correspond to considerably lower odorosity levels. A quantitative model for odor emission from resting dredged material probably could be developed if depletion rates at different air flow rates were measured.

Odor at disposal site boundaries

Some odor regulations specify permissible odor levels at the boundary line of the property that contains the odor source. The usual odor measurement device for odors in the field is a rather

primitive Scentometer (Gruber, Jutze, and Huey, 1950). Typical regulations may require that odor should not be noticeable at the lot boundary at a Scentometer setting of $D/T = 2$, or $D/T = 7$, or some other value. A few regulations simply specify "no odor."

Recently, calibration of the dynamic-triangle olfactometer vs. the Scentometer became available (Dravnieks, 1976). A Scentometer setting of $D/T = 2$ was found to correspond to 4.8 odor units by the dynamic olfactometer used in the present study. Only in one case, Point C at Anacortes, Washington (Table 35), was this value of 4.8 exceeded. This sample was taken downwind from a water surface covered with algae just in front of weir intake (Figure 19). The value probably reflects a secondary odor, that of algal decomposition, rather than the primary odor of the dredged material.

Odor character

Gasoline-like, oily odors were dominant in the Buffalo, Houston, and Detroit samples, with kerosene odor notes in the last two. Sour, pungent, and acid odor notes were present in the Milwaukee, Detroit, and Anacortes samples. The Mobile sample (an inactive site) and the York Harbor sample differed from the others by the absence of gasoline-like and sour/pungent odor notes. The Mobile sample had higher sweaty/rancid/animal characters than the other samples. Sulfidic odor notes were present only in the York Harbor, Houston, and Anacortes samples. These differences indicate possible differences in the genesis of the **odorants** and suggest that different oxidants or odor modifiers may be needed to control odors at different sites.

Of particular interest is the presence of household-gas-like notes in the Milwaukee, York Harbor, Houston, and Anacortes samples. Such odors may interfere with detection of gas leaks in households. Gasoline-like odors may similarly interfere with the detection of gasoline leaks in cars or other equipment.

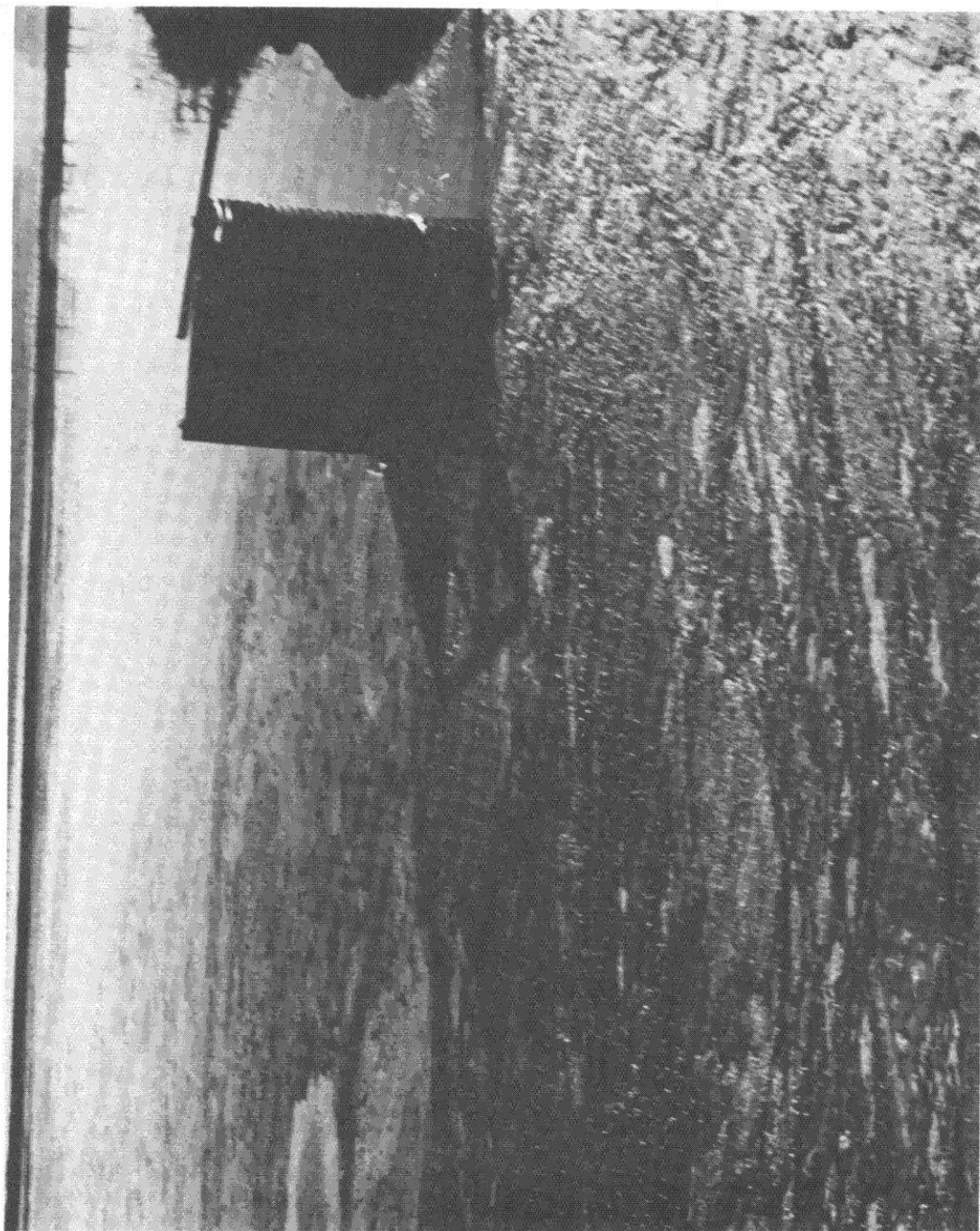


Figure 19. Scum on water surface around overflow weir, Anacortes, WA.

Effectiveness of odor counteractant

Table 25 indicates that at Houston, the odor unit content downwind of the odor counteractant was not influenced by the addition of the substance. Table 21 indicates that aromatic odor notes began to appear in the downwind odor: gasoline-like, household gas, and sewer odor notes. Some other odor notes decreased, but musty, burnt, and oily odor notes were enhanced. Thus, the essential odor character was modified, hiding some characteristics and promoting others, less characteristic by themselves.

There were several auxillary observations associated with the use of the fragrance solution. The counteractant, or its kerosene carrier, apparently worked as an insecticide. Many dead insects were seen in the vicinity of the mixture's storage drum. Soil just outside of the dike apparently stored significant amounts of the fragrance, because when a tractor passed through this area, the disturbed soil emitted the additive's characteristic odor. Ecologic consequences of systematic administration of a fragrance should be considered when liquid counteractants are employed.

Summary

In none of the sites were significant odorous problems observed beyond the diked area. A similar conclusion was drawn from analysis of the odor measurements and from a comparison of the measurements with values quoted in some typical odor-control regulations. This does not exclude the possibility that severe odor episodes may occur occasionally if particularly odorous dredged material is encountered. In some cases, the odor character may pose potential problems by masking the occurrence of leaks of household gas or gasoline.

Biological Origin of Dredged Material Malodors

Observations and interviews at the seven disposal sites suggest that odors associated with dredged material probably arise in two ways: (1) by release of odorants pre-existing in sediments during the **pumpout** of dredged material; and (2) by the de novo, in situ synthesis of odorants within the dredged material after its emplacement in the disposal site.

Odors were often detectable at nonactive locations or at active sites prior to **pumpout** of new material. Such odors were especially detectable during warm weather and were often dissimilar to those observed during pumping. For example, at Mobile, Site I, a "marshy" and "sulfidic"* odor was clearly discernible even though the disposal beds had been emplaced for about 3 years; the local removal of approximately 10 to 20 cm of surface material at this site exposed strata having a very unpleasant and strong odor of hydrogen sulfide. At Houston, prior to pumping, at a location about 200 feet from the discharge area, the following odor notes were sensed: "dirty mud," "sulfidic, " "petroleum-like," and "proteolytic."** Yet, the only discernible odor note at the pipe mouth during pumping was "petroleum-like." At York Harbor, a light, unpleasant, sulfidic odor was noted in an older disposal area, about 500 feet upwind of the active area. Observations such as these lead to the conclusion that there are two different classes of odors associated with dredged material disposal sites: those odors that issue essentially instantaneously from the pipe mouth during discharge operations and those that can be described as the background odors at the various sites.

The origin of some of the odorants released during dredging and pumping is fairly obvious. As discussed in Appendix A, sediments containing organic matter also contain the by-products of anaerobic

*Meaning "hydrogen sulfide-like."

**Like bacterial putrefaction; the sickening smell of rotting meat or fish.

bacterial decomposition (putrefaction), including H_2S and sulfur-containing organic compounds. Also present are certain fatty acids, aldehydes, **amines**, and other odorous substances. Industrial wastes may be present. Gas contents of dredged material can range up to 70% or more (Harrison, et al., 1964). When such sediments are disturbed by the dredge cutting head and experience further disturbances such as agitation, pressure changes, and pump cavitation, a large percentage of the odorous gases is released to the air at the mouth of the discharge pipe. Additional odorants, perhaps including some which are less volatile, are probably released to the air by the mechanism of aerosolization as the dredged material spews out and splashes against the surface of the disposal bed.

The origin of background odors characterizing some disposal sites is less easy to conceptualize. The following mechanisms, however, seem reasonable:

a. Under certain conditions (e.g., during or following warm weather), the more volatile **odorants** originally contained in the sediments (or their oxidation products), escape from the surface layers of dredged material beds to the air. It is likely that **odorants** at the very surface, especially the more volatile ones, are exhausted in relatively short periods of time.

b. Similar pre-formed odorants, located more deeply in the volume of dredged materials, are eventually brought to the surface.

An examination of the bacteriological results contained in this report reveals that a number of species found in the dredged material produce gas as a by-product of their metabolism. While carbon dioxide is the principal gas produced in the laboratory in glucose media such as this study employed, a number of other gases are commonly produced by bacteria in nature, including ammonia,

carbon monoxide, hydrogen,* hydrogen sulfide, methane, nitrogen, and others. Gas production in sediments has been discussed by Conger (1943), Kleerekoper and Grenier (1952), Marshall (1962), Howard (1971), Chen (1972), and Mallard and Frea (1972).

Bubbles of gas were observed breaking at the water surface over parts of the dredged material at the Mobile, Buffalo, York Harbor, Anacortes, and Houston disposal sites. It was not determined whether the escaping gas was hydrogen or "marsh gas" (principally methane), or if it had a different composition. Workers at the sites reported that the gas burns, suggesting that it is probably hydrogen and/or methane. The presence of the gas bubbles suggests the existence of conducting channels extending from deeper strata of the dredged material to the solids and water column interface. Furthermore, it seems likely that such channelization occurs throughout most disposal areas containing organic matter, whether covered by water or not, provided that the disposal material is not in a highly dessicated state or frozen; the presence of standing water only makes the release of gas and the existence of channels more evident.

**Escherichia coli*, a common intestinal resident of mammals found wherever man is found, is well known as a producer of hydrogen as a result of its action upon carbohydrates through a formic acid intermediate. Since *E. coli* is ubiquitous, it was not specifically looked for in the dredged material samples, its universal presence is assumed because of (a) the proximity of human beings to all dredging operations sites, (b) the proximity of sewage outfalls to some of these sites, and (c) the fact that associated enteric (intestinal) bacteria were identified in significant numbers at the Milwaukee, Mobile, York Harbor, and Houston sites, and in small numbers at the Buffalo site. While almost no ordinary enterics were found in the Anacortes sample, the presence of *Alcaligenes*, *Proteus*, and *Staphylococcus* suggests the presence of human contamination as these organisms are found in association with man. For these reasons, the authors believe that it is quite likely that bacteria capable of producing hydrogen were present in virtually all dredged material samples that were examined.

Thus, at some sites, bacterially-produced gas, moving upward through the dredged material, seems to act as a carrier for pre-formed **odorants** and brings them to the atmosphere during appropriate meteorological conditions. Additional discussion concerning gas production appears below.

c. Newly synthesized odorants, produced in the disposal beds principally by bacterial action, are carried by gases to the surface where they enter the atmosphere; as in the second mechanism proposed above (b.) the carrier gases are themselves the products of bacterial action.

A detailed discussion of bacterial aerobic and anaerobic metabolism (putrefaction) and the consequent by-products is beyond the scope of this report; however, it is commonly known that a number of odorous substances are produced, including hydrogen sulfide and odorous organic sulfides such as the lower mercaptans and diethyl sulfide (identified at the Buffalo and Grassy Island sites), as well as certain odorous fatty acids, esters, and branched, multiple, double-bonded aldehydes. While it is likely that a number of such substances are produced and present within the dredged material of disposal areas, hydrogen sulfide was the most readily identified **odorant** at the sites visited in this study. A number of parallels probably exist between the production of hydrogen sulfide (and other sulfides) in disposal areas and that produced in the hydrosphere. While a considerable body of knowledge is available concerning production of such compounds in the hydrosphere, little is presently known about their production in dredged material. Hence, a general discussion of hydrogen sulfide production and attendant microbial relationships is presented below.

An examination of the bacteriological data contained in this report suggests that complex, synergistic ecological relationships may exist among the disposal-bed bacteria, leading to the formation

of odorless gases that then act to form carrier-conduits for bringing odorous substances such as H_2S to the surface. Two general categories of bacteria were identified: facultative species (i.e., those that can grow either in air containing normal amounts of oxygen, or in media partially deficient in oxygen), and strict anaerobic species (i.e., those that can grow only in the absence of oxygen). While varying rates of gas production (not including H_2S) were observed in the laboratory in pure cultures of the facultative organisms, several isolates of strict anaerobes (*Clostridia*) were observed to produce voluminous amounts of gas over short periods of time. In the disposal beds where the organisms exist not as pure cultures but in various ecological relationships, it is highly likely that the activities of various groups of microorganisms influence the growth and metabolic activities of others.

For purpose of illustration, consider the Mobile disposal site (Table 13), where H_2S characterized the background odor. Here it is seen that at least two facultative species are present that produce H_2S : *C. freundi* and *P. mirabilis*. In addition to producing H_2S , these organisms produce other gases. A strictly anaerobic *Clostridium* Gp 3 species was also found to produce significant quantities of gas. At the site, it is logical to assume that the upper layers of the disposal bed contain active facultative organisms such as *C. freundi* and *P. Mirabilis* but not many active *Clostridia*. Conversely, deeper strata ought to contain fewer active *C. freundi* and *P. mirabilis*, but many active *Clostridia*. The events leading to this type of distribution relate to the influence of oxygen on the bacteria. The *Clostridia* could not grow in the uppermost strata where atmospheric oxygen could penetrate by diffusion; conversely, the facultative organisms could not thrive in deeper strata isolated from atmospheric oxygen, where a very low E_h would be maintained by the metabolism of strict anaerobes like *Clostridia*. In a situation such as this, we may visualize the production of H_2S by organisms in the more shallow strata, carried to the surface to some extent by

the facultative gas producers, but perhaps to a large extent by the deeper *Clostridia*. If H₂S producers were also present among the strict anaerobes (Table 4, *Clostridia* Gp 2) it is likely that H₂S produced in the deeper strata would be carried upward to the atmosphere as well as that generated by other organisms nearer to the surface. Not even considered in this illustration are relationships involving other classes of organisms such as the fungi, which are known to be extremely important in microbial ecology. Thus, the illustration must be considered to be highly simplistic.

However, if ecological relationships such as those predicted above do exist, it follows that their disruption can alter the normal production of odorous air above disposal beds. For example, periodic aeration of upper strata (say to a depth of approximately 1 foot) would be likely to decrease gas production by *Clostridia*, which, in turn, would decrease the mobilization of odorous substances to the atmosphere. This, in fact, may be one of the mechanisms involved in the reduction of noxious odors observed after aeration of disposed material containing organic matter and may also be one of the mechanisms involved in odor reduction in the field through treatment with oxidizing agents.

ANALYSIS OF METHODS OF ODOR ABATEMENT

The Operational Approach

Many of the most obvious and most cost-effective approaches to odor abatement fall under what may be termed the operational approach. For example, when dredging is to be done in sediments believed to be capable of producing malodors, samples should be taken sufficient to determine odor presence, type, intensity, and three-dimensional extent in the body to be dredged. The use of odor panelists should suffice for this purpose.

Once the malodorous features of a dredgable sediment body have been documented, it becomes possible to schedule the worst (in terms of production of malodors) portion of each dredging job for those periods when malodors from dredged material pumpout will least affect the surrounding population. For example, the most odorous part of a body to be dredged could perhaps be scheduled for the cooler months, when people are indoors more of the time, when the biogenic production of malodors is less significant, selecting conditions when atmospheric dispersion coefficients are higher. If a layer of thin, organic-rich and malodorous deposits existed in the upper few feet of the central portion of a sedimentary body scheduled for continuous 24-hr dredging, it might be possible to dredge the malodorous part of the body only during those hours when the land/sea breeze was blowing offshore.

Should it not be possible to program the dredging and disposal operation as described above, other methods of dredged material pumpout and disposal site management can be used to reduce odors. In the case of a pipeline dredge operation; for example, the dredge is often much farther removed from people who will be affected by dredged material malodors than is the diked disposal area. Inasmuch as it is the dredge pump that, by its thorough churning of the dredged material/water mixture, liberates great quantities of malodorous gas, it would be helpful to have a gas-ejector system on the pump.

The assumption here is that a significantly high percentage of malodorous gas would be released at the dredge far from easily offended, human olfactory systems. Gas removal systems are integral parts of hopper dredges (U.S. Department of the Army, 1954, p. 283) and should be considered for certain pipeline dredge operations.

It also may be possible to place the discharge end of the **pumpout** pipe under water, at least during the early phases of filling a diked disposal site. This would eliminate the spewing of the dredged material slurry into the air with attendant reduction in the vaporization of malodorous waters and liberation of contained gases. Overflow weirs should also be smooth, wide, and of limited depth to prevent excessive flow turbulence and associated liberation of malodorous gases.

Use of Olfactory-active Additives

Perception of a malodor can be influenced by injecting vaporous compounds into the ambient air so they reach odor receptors in the nose simultaneously with a malodor. For usefulness in malodor control, **the** resultant modified odor should be weaker, or less recognizable, or both. Cases in which a nonodorous substance modifies an odor are so far unknown; all known modifiers of odor intensity and character exhibit an odor of their own. Such a method of odor control is relatively inexpensive, and its various aspects deserve a detailed consideration.

Claims that some additives neutralize odors by actually removing odorous substances from their free vapor state in air are untenable. Such claims are inconsistent with the chemical kinetics of reactions of dilute vapors in air. In one case that an author (Dravnieks) of this report has studied, analytical measurements were conducted on odorized air before and after addition of a certain neutralizer; analytical change in the **odorant** concentration was within the limits of analytical error, while the change in the perceived odor was

unmistakable, indicating that the effect is sensory rather than chemical. Even an oxidant as active as ozone significantly depletes the concentrations of readily oxidizable odorants in the vapor phase only after contact for many hours or days (Gotlauf and Berger, 1969). Reactions with ozone in the water phase are much more useful.

Basically, any substance that would be active enough to react with odorants in a very dilute state in air would be most likely to interact also with biochemicals in the human body and be potentially harmful to human beings. Odor-control chemicals that deaden the sense of smell, such as formaldehyde used in old formulations, are unacceptable for odor control because they interfere with the warning odors and the enjoyment of flavors.

The use of air-dispersed (or added-to-the-source) odor modifiers increases air pollution. Therefore, this method of abatement should be limited to occasions in which distinct malodor problems exist, and sufficient evidence is available that the additive will mitigate the malodor. Also, formulations used for malodor abatement should not contain toxic, carcinogenic, or mutagenic components.

Various aspects of odor-control technology involving the addition of volatile formulations are now discussed, a scientific classification of odor-interaction effects is presented, and comments are made on the commercial terminology, safety, and economical factors that should be kept in mind when considering use of this method for abatement of malodors. Finally, an actual case involving use of an odor-modification system is described.

Scientific classification of odor interactions

Sensory interactions between a target malodor and an odor modifier are best classified in quantitative and qualitative terms based on present-day concepts of sensory psychology. Such a classification can be found in a paper by Cain and Drexler and is systematized in Table 38 using their terminology.

Table 38

Classification of Effects in Sensory
Interaction of an Additive and
a Target Odor

Definition of Symbols:

T = odor intensity of target odor; e.g., malodor.

A = odor intensity of additive vapor.

TA = odor intensity of the mixture of both.

(It is assumed that $A < T$)

Quantitative Effects

- | | | |
|----------------------|----------------|-----------------|
| 1. Hyperaddition | $TA > (T + A)$ | |
| 2. Complete addition | $TA = (T + A)$ | |
| 3. Partial addition* | $TA < (T + A)$ | |
| 4. Compromise* | $T > TA > A$ | "COUNTERACTION" |
| 5. Compensation* | $T > TA < A$ | |

Qualitative Effects

- | | |
|------------|----------------------------------|
| 6. Masking | Odor of T not recognizable in TA |
|------------|----------------------------------|

Combination of Quantitative and Qualitative Effects

- | | |
|--------------------------------|----------|
| 7. Masking with addition | $TA > T$ |
| 8. Masking with counter-action | $TA < T$ |
-

*Forms of Hypoaddition.

In Types 1 and 2, the odor of the mixture is equal to or stronger (hyperaddition) than the sum of the odor intensities of the components. In Types 3 and 7, the odor of the mixture is still stronger than that of the strongest components, but weaker than the sum of both (hypo-addition). In Types 4 and 8, the odor of the mixture is weaker than that of the stronger component (in this case, of the target malodor), but stronger than that of the weaker (additive); in Type 5, the odor of the mixture is even weaker than that of the weakest component and is termed compensation.

Effects useful for malodor control are limited to Types 4, 5, and 8. Even Type 7, if the resultant odor is more acceptable but only negligibly stronger than the malodor, may have usefulness in reducing odor complaints.

Masking by overpowering with a stronger odor is undesirable, while masking with counteraction is the most desirable form of odor control. However, suppliers of odor-control additives avoid using the term masking altogether, because of its presumed connotation of hiding by overpowering.

Existence of the counteraction sufficient to be termed true compensation, Type 5, has thus far not been supported by an quantitative study (First, 1958; Kerka, 1961; Jones and Woskow, 1964; Köster, 1969; Cain and Drexler, 1974; and Dravnieks, 1976).

In quantitative controlled studies, the extent of the useful control of a malodor by additives was invariably limited to a *change in the character of odor, with or without a decrease in the sensory intensity of the malodor*. The odor character of the additive when in the mixture may also undergo change, but so far the odor intensity has never been found to be less than that of the additive by itself.

Measurements of the effect of the counteractant used at the Houston dredged material disposal site showed that the Houston case

also fits into the above type; that is, there was some change in odor character, but no significant change in odor intensity.

Commercial Terminology

Commercial organizations that offer specific formulations for the control of various malodors have generated a somewhat confusing, sometimes self-serving, nomenclature that suggests their presumed mode of action. Usually, the manufacturers support their claims by case histories and testimonials rather than by quantitative sensory data. Terms used to describe the odor-abatement substances include:

- odor modification
- odor counteraction
- odor neutralization
- de-odorization
- re-odorization (i.e., replacement of odor)
- odor masking
- air freshening
- air restoration

Odor modification is the least pretentious and most acceptable of the terms, since it implies possible changes in the odor intensity and character.

Counteraction, neutralization, and de-odorization imply to the consumer that the odor-control formulation somehow does away with the malodorant molecules, although the most it can do is simply to modify the odor perception generated by malodorant molecules.

Re-odorization rationalizes further, implying that an odor (the odor of the added formulation) is somehow capable of dealing with the original malodorant molecules so that the resulting odor is a pleasant one.

Odor masking is a term abhorred by most manufacturers of odor-control formulations. Created by distributors, the term implies covering the malodor with a much stronger pleasant odor. In reality, masking involves making the malodor unrecognizable and may be

accompanied by a change in the odor intensity, either up or down.

Air freshening means imparting a pleasant weak aroma to air, with suppression of the pre-existing malodorous notes. This term is usually reserved for the treatment of inside air.

Air restoration is a term implying the pleasant notion that all malodorous and other odorous molecules have been "removed." Again, such effects are still within the classification given in Table 38.

Safety aspects

Emission of the vapor from odor-control formulations adds to the exposure of the population to chemicals. Consequently, some odor regulations prohibit this method of malodor control. Certain others go along with this method on a temporary or emergency basis.

Two principal health hazards may exist. One hazard is readily assessable by sensory tests. Gas leaks, incipient fire, overheated electrical motors, etc., generate warning odors. Buildup of such odors may be either gradual or rapid. It is undesirable that odor-control additives modify such hazardous odors significantly. A controlled study of the extent of such effects is not known. However, the contribution of indoor air fresheners to hiding gas-leak odors has sometimes been questioned in investigations of explosions caused by gas leaks.

Early deodorizing formulations contained compounds that deadened the sense of smell. Clearly, this approach to modifying odor perception is unacceptable. The other potential health hazard is much more insidious. Lists of compounds found potentially carcinogenic or mutagenic (causing birth defects), or both, are growing rapidly. Many substances considered harmless in the past are now being reclassified into such lists.

Arguments are usually advanced that the components of the additives are natural substances or are on the official GRAS list (Generally Recognized As Safe) for use in human consumption and are used at very high dilutions. Also argued is that for years the General Services Administration has accepted the use of room air fresheners and has even published test procedures for evaluating their efficiency in the control of malodors (Federal Specifications, 1974).

Such arguments are weak because of the lack of solid information on the actual composition of the additives and the potential carcinogenic and mutagenic properties of the components. Surely there are many quite harmful natural substances; and occasionally compounds are removed from the GRAS list because new work shows their potential harmfulness. Also, because of the complexity of the composition of most odor modifiers, as is readily obvious from gas-chromatographic analyses of their vapors, it is very doubtful if any one can really supply reliable composition data for their formulations, save in the grossest sense.

Economic aspects

The addition of vapors from odor-control formulations to air at the downwind periphery of a dredged material disposal site is potentially more economical than chemical treatment of the dredged material itself. Three factors related to the economy of such a method deserve discussion.

First, some experience with odor control by additives in other applications have shown that after using this method, the odor complaints drop, but then rise again; people begin to associate the same odor source with the new odor. For example, this has occurred in attempts to control diesel-bus exhaust odors by fragrant additives to the diesel oil in a metropolitan area, and in attempts to control human body odors in metropolitan public transportation vehicles. Due

to the transient nature of the dredging operations, however, such a relapse may not occur.

A second factor relates to economical operation of the odor-control system. Frequently, once the system is installed, it will be operated most of the time "just to be safe," irrespective of the actual need at any given time.

The third factor is a hidden one. Objections may be raised against discharging chemically undeclared materials into the atmosphere. This could lead to costly litigations. It would perhaps be proper if the suppliers of the formulations would be required to carry out the costs of such litigations.

Commercial use aspects

Odor modification has been defined by industry (Elinsky and Lauren, 1974) as "the process whereby, when two substances of given concentrations are mixed, the resultant odor of the mixture may be far less intense and objectionable than that of the separate components and may not even be perceptible." For purposes of abatement of malodors associated with area sources, odor modification is accomplished by the introduction of vapors via blowers and perforated pipes (Cheremisinoff, et al., 1975) placed along the periphery of the offending source. The substances employed in odor modification are specifically designed formulations of aromatic compounds. These compounds are sold commercially and all formulations are proprietary. Systems for odor modification have been installed to treat emissions from entire plants, waste treatment ponds, refineries, and related sources.

Of interest to the present study is the odor-modification program currently employed by the Sewerage Commission of the City of Milwaukee, Wisconsin. The program is applied at the South Shore Waste Water Treatment Plant located in Oak Creek, about 10 miles

south of the Jones Island Plant (Figure 7). Musty and sewage-like odors are modified with Photonic Environmental Corporation's Odor Modifier 810154. This substance consists predominantly of terpenes with small amounts of essential oils and aroma chemicals added. The use of this odor modifier complies with all existing local, state, and federal regulations.

Odor modifier #10154 is dispensed by the system shown schematically in Figure 20. Two ducts, each 610 ft long, convey the modifier gas along the periphery (Figure 21, A) of three sides of the odor source. Malodors from about 25 acres of sludge-holding ponds are thus controlled. The rate of introduction into the ducts is equivalent to approximately 7 oz of liquid per hour.

As seen in Figures 21 and 22, the odor source of the South Shore Wastewater Treatment Plant is in close proximity to a subdivision of homes. Prior to installation of the odor-modifier system, there had been a history of numerous and sometimes vehement complaints. Subsequent to the odor-modification program, which began July 31, 1975, only one complaint was received (J. R. Grinker, 1975, oral communication). One of the authors (Harrison) visited the site on November 12, 1975, when a brisk breeze from the WSW and SW quadrants was blowing across the holding ponds (Figure 22B) and into the southeastern section of the subdivision. The expectable malodor was perceived within the holding-pond area. Immediately downwind of the duct, and in the subdivision, however, the malodor could not be detected. Discussions with personnel of the South Shore Wastewater Treatment Plant indicate that the most difficult test of the odor-modification system will come in the late spring of 1976, when odors from the sludge-holding ponds reach a peak.

The sewage-like malodors at the Milwaukee disposal site (Figure 7) originated from sediments dredged within a few hundred feet (Figure 7, B) of the Jones Island Sewage Treatment Plant. As a

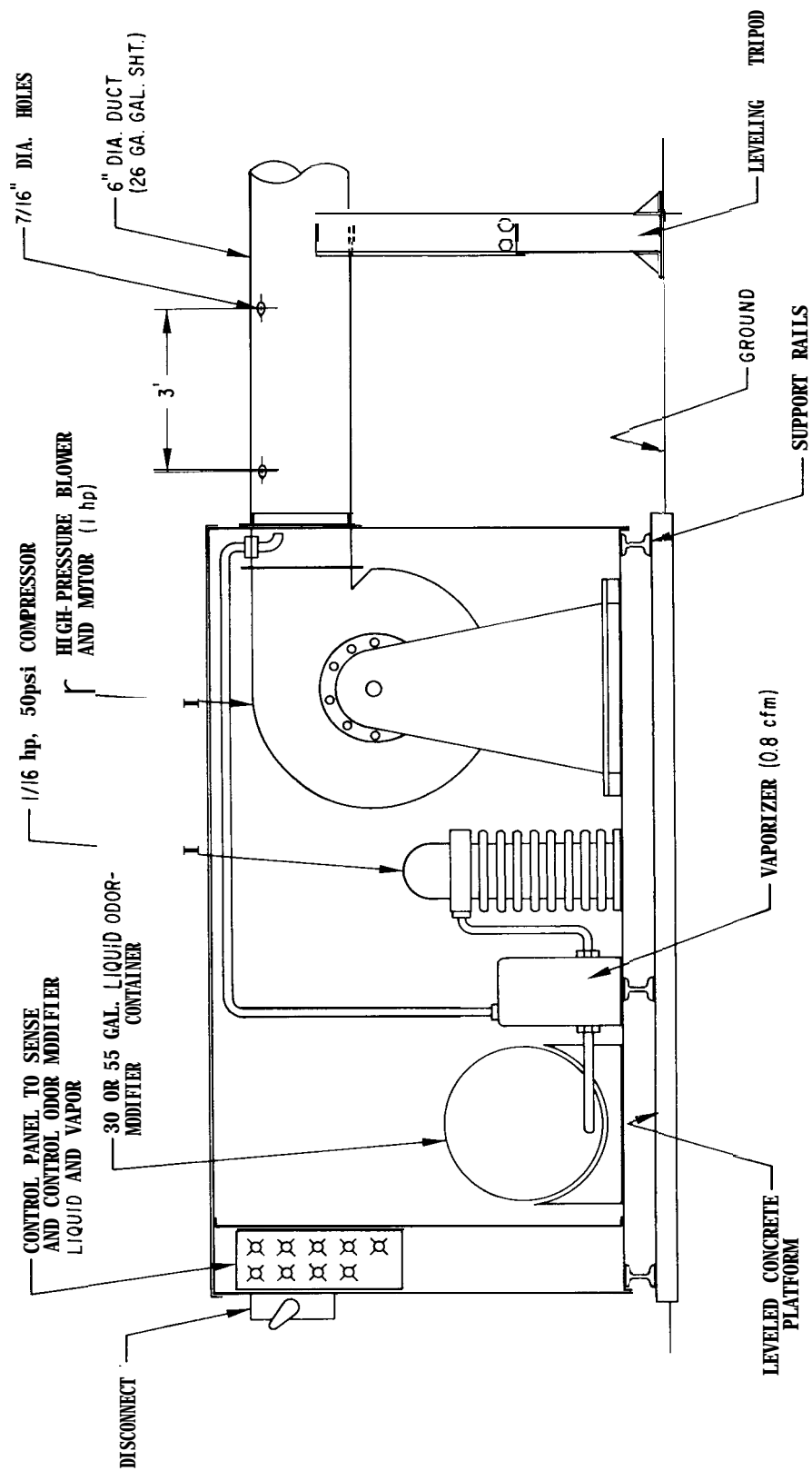


Figure 20. Schematic diagram of odor-modifier control and dispensing station.

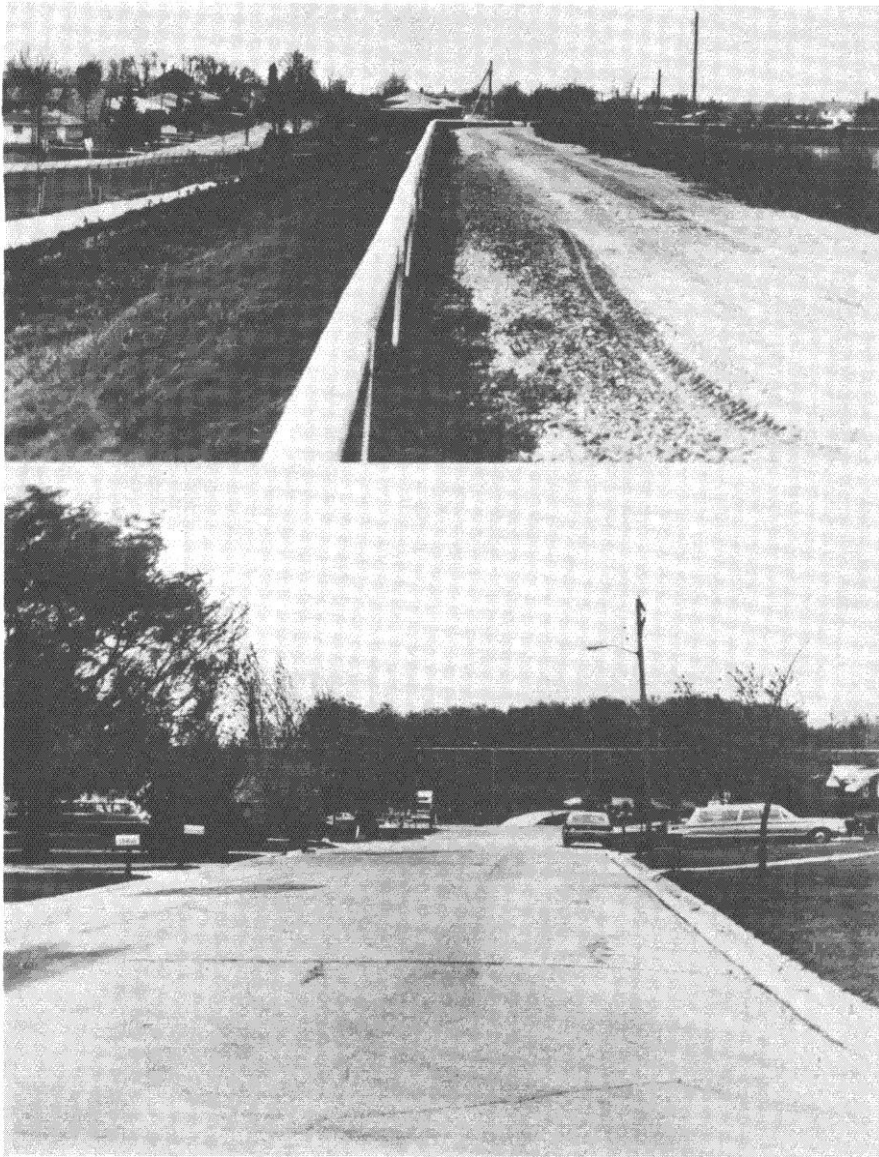


Figure 21. A. Duct for conveying odor-modification gases along the perimeter of the diked sludge-holding ponds at the South Shore Plant, Milwaukee. View is toward the north.
B. View of duct from subdivision on north side of diked sludge-holding ponds. View is toward the south.

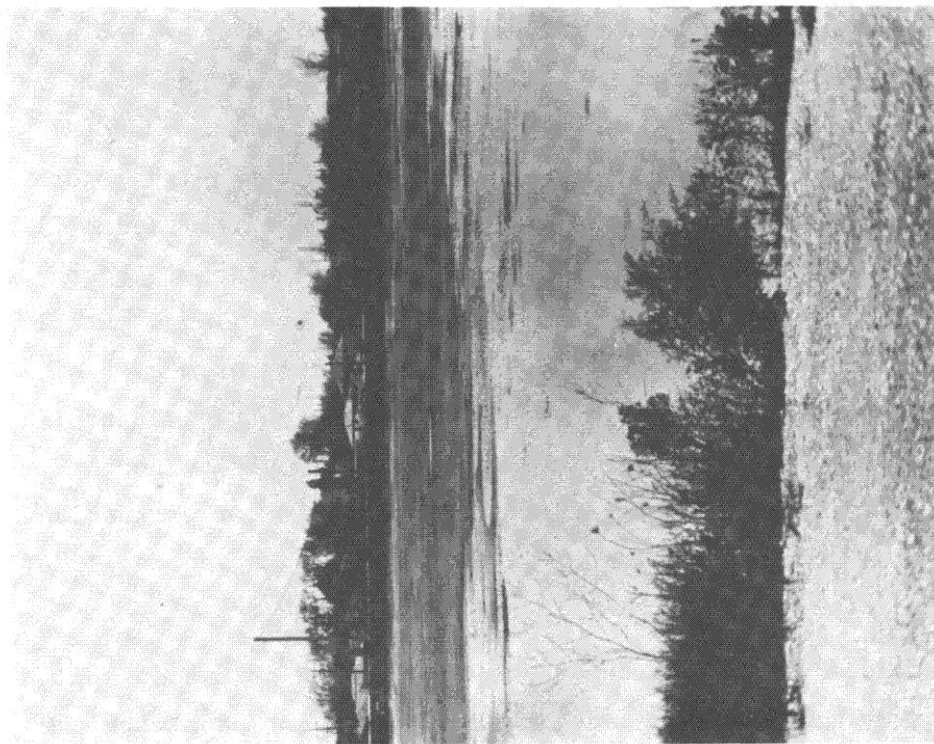
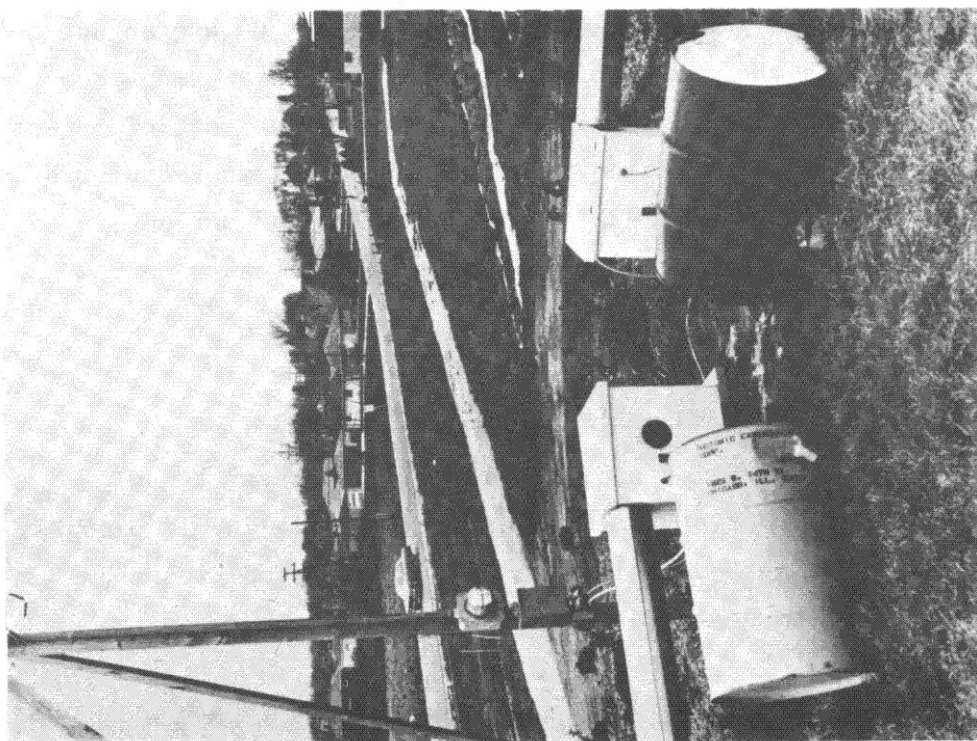


Figure 22. A. View of barrels of liquid odor modifier, blower housings and ducts at Milwaukee site. Lefthand barrel visible in center of Figure 21, A.
B. View of sludge-holding pond and duct at Milwaukee site looking northward.

hypothetical example of the use of odor modification, consider that if sewage-like malodors can be abated successfully at the South Shore Plant's holding ponds, only 10 miles south of Jones Island, it ought to be possible to abate similar sewage-like odors when they occur at the Milwaukee confined disposal site (Figure 7). The odor-modification system at the South Shore Plant cost about \$2.00 per lineal foot to build in 1975. This cost reflects materials only. Using 1975 dollars, and allowing for the increased size of the Milwaukee dredged material disposal site, the cost of installing a perimeter system along three sides of the site would be about \$9,600 at \$4.00/lineal foot for 2,400 feet of perimeter protection. Operating costs would approximate \$1,200/month (O. B. Lauren, 1976, oral communication).

As discussed earlier in this section, masking of malodors is accomplished by mixing a substance having a pleasant odor with the substance producing the malodor. This results in a different and more pleasant odor than that experienced initially. At the Houston diked disposal site, for example, Custom Industries' "Counteractant No. 11" is mixed with the stream of dredged material emanating from the pipe. The counteracting odor is described as being that of "sweet pine" and is diluted with kerosene. According to the manufacturer's specifications, "Counteractant #11 is a select blend of perfume, counteractants, and surfactants designed to promote cleaner and healthier living."

Use of Oxidants and Aeration

Treatments by ozonization and aeration do not appear to be promising methods for odor abatement. Dredged material would probably be treatable by these methods only when in a slurry condition and it will be difficult to generate an efficient contact between the gas and slurry phases.

The results with other oxidants were reasonably promising, with KMnO_4 , H_2O_2 , and NaOCl most possibly able to reduce odor level, in terms of ED_{50} values, by a factor of 2 to 3. Of particular interest is the observation that higher concentrations of the oxidants were not significantly more efficient than low concentrations. Thus, a small addition of an oxidant appears to oxidize some of the more odorous components present in the dredged material. Because the present odor survey at disposal sites indicated that the odor problem was marginal, an improvement by a factor of 2 or 3 could often be sufficient for reducing the possibility of malodor complaints.

The effect of lime was not significantly evident in the laboratory tests. In the case of dredged material containing the equivalent of sewage sludge, however, lime may be of value because it has often been used to control odors from dewatered sludge applied to land (U.S. Department of the Interior 1968, p. 306).

Odor complaints are influenced not only by the odor intensity but also by the odor character. Oxidants had a slight influence on the odor character of the Grassy Island dredged material, possibly influencing principally the kerosene-like odor note. The full effect of oxidation treatments on the odor nuisance potential of dredged material samples cannot be determined in small laboratory-scale experiments, and can be tested adequately only in large, on-site experiments.

Since the character of odors changed with the type of the dredged material, the relative efficiency of different oxidants may depend on the type of the dredged material. Approximate evaluation of the relative efficiency of various oxidants in treating the particular type of dredged material can be conducted in the laboratory. Tests should be limited to the relatively low-level addition of oxidants, conducted on a sufficient number (4 or more)

of untreated samples and a sufficient number (5 or more) of subsamples treated with a given oxidant. Oxidants most active with respect to the particular material should be selected for field trials.

It should be noted at this point that unless all of the odor-producing substances are destroyed by a treatment method, the odors remaining may be as strong or as objectionable as the initial odor. In addition, the odor *quality* may change with atmospheric dilution (or diminution of source strength through the use of oxidants). In a mixture of odorants, this may be because one odorant is more pervasive than the others. A high concentration of trimethylamine has an "ammoniacal" odor, for example; but at low concentrations, the odor is "fishy." The reason for these differences is not fully understood (Summer, 1968).

The results of the experiments (Table 36) with oxidants and aeration reveal some erratic variations of odor-threshold levels (ED_{50}) as a function of time, which may in large part be due to experimental variables that were difficult to control. Among such variables would be laboratory air temperature and the unequal loss of odorous vapors during transfer of different experimental samples from sample-preparation or sample-storage containers to the Tedlar bags used for the odor-panel tests. An additional explanation for the results (Table 36) may lie in the very nature of determining the threshold concentration of odors. Although the concept of an odor threshold implies a simple determination of presence or absence of an odor, thus leading to a simple form of quantification, there are a number of factors that can affect threshold values.

Experience Abroad

As part of the effort to survey the state of the art of odor abatement, letters were sent to professional colleagues concerned with odor problems in other countries. The following responded:

Dr. L. Molhave, Institute of Hygiene, Aarhus University, Denmark;

L. W. Hansen, Fläkt Luftteknik, Denmark;

K. Varnoe, Ministry of the Environment, Agency of Environmental Protection, Denmark;

S. Dalager, Envioplan A/S, Denmark;

Dr. H. N. M. Stewart, Warren Spring Laboratory, Department of Trade, Great Britain;

Dr. P. Degobert, Laboratory for Odor Studies, French Petroleum Institute, France;

Dr. B. C. J. Zoetman, National Institute for Water Supply, Netherlands;

Dr. L. J. van Gemert, TNO Institute, Netherlands;

Dr. E. Eggink, Central Environmental Protection Agency, Rijnmond, Netherlands;

Dr. T. Lindvall, Department of Environmental Hygiene, Karolinska University, Sweden; and

Dr. D. G. Laing, CSIRO, Australia.

Some of the above communicated with other specialists, including members of agencies responsible for maintaining navigational waterways in their countries. The information obtained from the various parties is summarized below. In general, malodors at European dredged material disposal sites do not constitute a serious problem, except when pockets of industrial wastes occur in the areas undergoing dredging.

a. Australia: Odor problems have not yet arisen.

b. Denmark: Disposal is at sea or on land away from population centers; odor problems have not been encountered.

c. France: Dredged material from harbors is disposed in the open sea. Material from inland waterways is disposed in diked areas along rivers away from population centers, not so much because of odors but to avoid mosquitoes and humidity. Odors from dredged material do not last long. Mechanical pressing of disposal material

between rollers is used to accelerate drying. The problem with odors from dredged material is not acute. The spraying of "walls" of aerosols containing masking agents was recommended if problems were expected with malodors.

d. Great Britain: Odor problems with dredged material have occurred on a very small scale and, allegedly, are controlled by counteractants or masking agents. Results are poorly documented. The evacuation of material for roadways in peak areas produces sulfidic odors which subside in a few hours.

e. Netherlands: Odors from dredged material become significant if the petroleum contents reach 1000 mg/kg and the weather is sunny with low wind speeds. When such material is encountered in dredging, it is disposed into the sea instead of on the land. A case of 150 complaints, all occurring on one single morning, was related to the passage of barges carrying dredged material, most probably containing acrylates, originating from an industrial plant. At that point, dredging was already finished and nothing else needed to be done. A case of 16 complaints in one day dealt with chlorine odor and irritation originating from a site where dredged material was deposited in preparation of sites for housing construction. The dredged material was traced to a part of the harbor where a chlorine handling industrial company apparently dumped some waste. Dredging activities in that part of the harbor were immediately stopped by the Rotterdam Harbor Authority.

f. Sweden: The Environmental Protection Board requires that sludge disposal areas should be on land for toxicological reasons and that possible odor emissions should be dealt with. In a very few occasions when odors from dredged material have been a problem, the odor emission has been reduced by adding calcium oxides to raise the pH. Other countermeasures, besides using another disposal

area away from populated areas, is to cover the disposal area with earth and sow with grass.

Application of Microbiological Principles

No microbiological method is suitable for abatement of malodors resulting from the instantaneous release of pre-formed odorants at the time of dredging and pumpout. For such malodors, the physical, chemical, and sociological abatement strategies proposed previously are most appropriate. For residual and background odors of biogenic origin, however, there are several strategies involving microbiological principles that might be effective in preventing or reducing such odors. The following paragraphs discuss the strategies of disinfection, antibiotic treatment, pH adjustment, microbial competition, and bio-conversion.

Disinfection

The use of disinfection to prevent bacterial growth and putrefaction is well established, and ranges from the simple process of adding chemicals such as chlorine to sewage-containing effluents, to the sterilization of medical instruments by immersion in alcohol. A number of chemical agents are known to control microbial populations, including high concentrations of salts such as sodium chloride; heavy metal cations such as borate and fluoride; halogens such as chlorine, iodine, and fluorine; oxidizing agents such as peroxides, permanganates, and ozone; surfactants such as soaps, synthetic detergents,, and quaternary ammonium compounds; phenols; dyes; formaldehyde ethylene oxide; and alcohols. The actions of these substances are summarized in some detail by Dubos (1958), Pelczar (1958), and Smith et al. (1957).

The proposed use of such agents does not constitute a new concept. High-organic wastes are often treated with sodium hypochlorite to destroy pathogens and reduce odor potential. A commercially available formaldehyde source called "Modocide" (Lauren, 1974) releases formaldehyde at a controlled rate governed by temperature and has been used to control malodors on a small scale, such as in swine-farrowing facilities. In water-treatment facilities, an increase in potability of odorous waters is routinely achieved through the use of oxidizers such as potassium permanganate. A potassium manganate compound called "odorex" has been used effectively to help eliminate the hydrogen sulfide odor emanating from various areas of a sewage treatment plant (Bernicchi, 1968). In cases where manganate oxidants are used, the immediate reduction in malodors is due to the oxidation of noxious contaminants to non-noxious substances; the residual abatement effects that doubtlessly occur also involve the control of bacterial populations. A method involving the use of hydrogen peroxide has also been found effective in the removal of noxious odors in wastewater treatment (Lindstrom, 1975) here, too, the **bio-cidal** effect of peroxide must certainly be involved in preventing the recurrence of the problem. Unfortunately, the use of hydrogen peroxide for the abatement of dredged material malodors would be very expensive. Other types of oxidation processes such as in "Cataban Process" (Lauren, 1974; and Bernicchi, 1968) also probably have a residual odor abatement characteristic through microbial population control, as well as the immediate beneficial effect of eliminating hydrogen sulfide.

Of the disinfectants mentioned above, only a few appear to be practical for large-scale, outdoor application to dredged material because of considerations of cost, toxicity, lability, quantity necessary, odor, corrosiveness, staining potential (e.g., that caused **by dyes**), and other factors. Thus, of the agents listed above, only chlorine (in the form of hypochlorite), formaldehyde (as the liquid

or as a slow-release chemical complex), and perhaps in some cases, cheap oxidizing agents and surfactants seem to be possible choices. For most effective application these would be mixed with dredged material in the discharge pipe prior to disposal.

Whatever the choice of agent and mode of application, an analysis of site-specific parameters and sediment characteristics must be considered in advance to determine suitability and cost effectiveness. This information must also be balanced against possible adverse environmental effects that may result from the use of the agent. Only in this way can the Corps of Engineers management determine if dredged material disinfection will be an appropriate odor-abatement method for a specific site or if alternative methods would be more desirable.

In any case, disinfection should not be considered as an ultimate method for the inhibition of background odors at disposal sites. Rather, disinfection techniques should be thought of as short-term remedies, to be followed by the more permanent procedures to be discussed later. The reason for this conclusion is the knowledge that since total sterilization of dredged material would not be cost-effectively feasible. Vigorous bacterial action would eventually be reestablished in any moist disposal area containing organic matter, because all common disinfectants would eventually be degraded by chemical and/or biological action and the remaining "seed" microorganisms would multiply to occupy the ecological niches existing at the time the treatment was begun. The time frame for such reversals to occur cannot be predicted here since they would involve a number of site-specific and elective parameters as well as the type of disinfectants used. Laboratory studies, followed by small field demonstrations, would be necessary to obtain the information necessary to make reliable predictions.

Although the use of disinfectants cannot be considered as a permanent odor-abatement strategy, some instances can be suggested

in which the empirical use of disinfection might be justified:

- a. If dredging contracts require that highly odorous upper strata be removed during the hottest weeks of summer, disinfecting of these materials during discharge would be likely to suppress the continued bacterial production of **odorants** until cooler weather would assist in suppressing bacterial action.
- b. In a case similar to the above, disinfection could serve to suppress bacterial odor production in the most offending dredged material until it could be covered over by other dredged material known to have less odor potential.
- c. At disposal areas characterized by good drainage and low precipitation, disinfection could serve to suppress bacterial odor production until the dredged material would become naturally dessicated to an extent where bacterial action would be minimal.
- d. Disinfection could possibly suppress bacterial odor production long enough (several weeks, perhaps) to allow other, more permanent strategies to take hold.

In summary, disinfection of dredged material may be useful as a temporary method of inhibiting the microbial production of malodors that might arise as a characteristic of disposal sites. Disinfection would not be very cost effective, however, and would be of value only for abatement of severe malodor problems where odor-modification systems could not be installed.

Antibiotic treatment

Antibiotics kill or inhibit the growth of microorganisms and have been used in this capacity to retard the formation of odors due to decomposition. For example, until such use was prohibited

by the U.S. Food and Drug Administration, antibiotics had, on occasion, been used to preserve meats and diminish the formation of putrid odors. There is also some precedent for the use of antibiotics to treat sediments of natural water bodies. Flegler et al. (1974), have used nystatin, cycloheximide, penicillin, and streptomycin to treat the sediments of Lake Lansing and Rose Lake Bog in Michigan in order to study the effect of fungi on organic decomposition. Their results indicate that antibiotics do have an inhibitory effect on bacteria and fungi contained in the sediments.

Nevertheless, based upon the costliness of antibiotics, the authors do not believe that cost-effective methods of treating dredged material with antibiotics can be developed. Other inhibitors of microbial growth discussed previously are comparatively inexpensive and should be considered in lieu of antibiotics when suppression of microbial growth in dredged material is desired.

pH adjustment

Most bacterial growth is restricted to a pH range of 5 to 9; however, optimal growth is restricted to a much narrower range, usually close to neutral.* For example, *Clostridium botulinum*, a strict anaerobe involved in food poisoning is typical of *Clostridia* species; it will grow only at neutral or slightly alkaline pH (Smith, et al, 1957); it will not grow under even moderately acidic conditions. The use of pH adjustment to inhibit bacterial growth has widespread application and need not be discussed further in this report.

An examination of Tables 5, 10, 14, 19, 24, 29, and 34 indicates that of the seven sites visited, five were characterized by dredged material having a neutral pH, while one was slightly acidic (pH 6) and one was slightly basic (pH 8). These pH ranges are favorable

*A notable exception being certain acidophils that can grow in and accumulate sulfuric acid up to several percent.

for the growth of most microorganisms; observations of escaping marsh gas at several sites indicated active bacterial metabolism. Consideration of this information strongly suggests that odors originating in dredged material as a result of microbial activity can be inhibited by controlling the pH. However, prior to the application of this method to any disposal area, the authors strongly recommend that controlled laboratory studies using dredged material (obtained from cores) and small field demonstrations be used to establish appropriate treatment parameters on a cost-effective basis.

While impure acids and alkalies are relatively cheap in commercial quantities and might be mixed into dredged material prior to discharge on a cost-effective basis, it may also be possible to adjust pH with acidic or basic materials usually considered wastes themselves; for example, strip-mine spoil, deep mine wastewater, smokestack scrubber wastes, and industrial wastes. Proximity between such waste sources and disposal areas would favor investigating the use of the concept; while distance would be a discouraging factor, portable slurry pipe transport of waste materials could reduce costs. Recent trends in regulation of environmental pollution suggest that waste-use concepts such as suggested above may eventually be encouraged by Federal and State agencies charged with the proper disposal of man-generated wastes.

Bacterial competition

As discussed previously microorganisms including bacteria live in complex ecological relationships. Factors such as local pH, availability of substrates (foods and growth factors), oxygen and carbon dioxide tensions, and inhibitory biochemicals are all strongly influenced by the presence of microorganisms. Because of this, the generation time and rate of growth of any particular cell is governed by other cells in the vicinity. Put simply, microorganisms in nature live in dynamic competition with each other. Thus, excessive growth

of one species inhibits the growth of others within its sphere of influence.

The practice of using bacterial competition to obtain a desired effect is well established. For many years, the dairy industry has made cultured milk products from milk not totally free of undesirable bacteria by flooding the culture with greater than normal numbers of the desired bacteria. In sewage treatment plants, bacteria-rich anaerobic sludge digesters have been started with an appropriate inoculation of microorganisms from established digesters. In homes, sour septic tanks have for years been remedied by the injection of commercial starter consisting of nothing more than desired strains of dessicated digestion bacteria in an inert carrier.

More recent developments concerning the industrial use of bacterial competition include marketing dried cultures of mutant bacteria for specific waste-treatment functions. An example of this is the "Polybac" process (Worne Biochemicals, Inc., Lyon Industrial Park, Route 73, Berlin, N.J., 09009), which floods the sewage of treatment plants with mutant aerobic and microaerophilic bacteria designed to reduce the biochemical oxygen demand (BOD) and to increase plant capacity by the accelerated degradation of lipids, detergents, and cellulose. The "Polybac" process has been used in activated sludge systems, trickling filters, and oxidation lagoons. Another example is "DBC plus" (Bower Industries, Inc., 1601 W. Orangewood Ave., PO Box 1631, Orange, CA., 92668), a mixture of saprophytic bacteria designed to seed waste-treatment systems with bacteria especially suited for the digestion of proteins, carbohydrates, and fats, in order to induce desired digestion characteristics into the treatment system as a whole. Both techniques have been applied to as diverse sources as the Lincoln Water Pollution Control Facility (Stockton, CA) and the Queen Mary Flagship for its management of oil wastes. The bacteria contained in their preparations do not have the capacity to produce hydrogen sulfide (written communication,

21 November 1975, Robert B. Grubbs, Manager of Environmental Divisions, Bower Industries, Inc., Orange, CA).

Although the authors have not been able to find a single instance in which concept of bacterial competition has been applied to dredged material disposal sites, the underlying principles appear to be sound and would be similar to those operating in the examples given above. Thus, by mixing fast growing mutant bacteria, known not to produce malodorants, with dredged material containing a variety of "wild" bacteria known to produce malodorants, an artificial competition would likely be induced, resulting in a measure of long-term control over background odor production. This concept should be tested in the laboratory and in field-demonstration projects using, initially, commercially available materials.

In the authors' opinion, the surface application of mutant bacteria would not be effective because biogenic odorants are probably produced in subsurface strata. Furthermore, it is not likely that the mutant strains could become permanently established at the air-solid interface. It has been recommended (Grubbs, 1975, oral communication) that the "DBC plus" be injected into the discharge pipe at a rate of 1 lb/10,000 ft³. The authors add that because of the gas-adsorptive characteristics of many dredged material it should not be necessary to treat the entire depth of the disposal bed. Rather, the bacteria should only be injected into that dredged material which will constitute the upper layer of the disposal bed. An optimum depth of treatment should first be determined on a cost-effective basis, using laboratory and/or small demonstration plots.

In lieu of using commercial preparations, non-proprietary organisms such as *Bacillus* sp.* could also be investigated in the laboratory and field to determine their effectiveness as a competitor of odor-producing, dredged material bacteria.

Bioconversion of malodorants to less odorous compounds

It is generally known that odors emanating from odorous dredged material can be reduced by covering the offending material with dirt, sand, or less odorous dredged material. Several of the mechanisms operative in such odor abatement have been discussed earlier in this report. This section will consider a specific bioactive overlay for odor abatement of hydrogen sulfide (the most common sulfurous odorant) as well as for some other odorants containing the sulfide moiety (those containing specific microorganisms that are known to convert sulfide to sulfate ion). This process is called "bioconversion."

An examination of Appendix A and Figure A-1 indicates that in addition to microorganisms (e.g., *Desulfovibrio* sp.) that convert organic materials and sulfate to sulfides, there are other microorganisms that utilize sulfide and produce odorless elemental sulfur or sulfates, both of which are odorless. Included in this group are the colored photosynthetic bacteria and colorless nonphotosynthetic bacteria such as *Thiobacillus* and *Beggiatoa* sp. (Hutchinson, 1957; Schwoerbel, 1971; and Dunnette, 1973). The bioconversion of sulfide to sulfate occurs not only in nature at various stages of the sulfur cycle, but in man's work as well, wherever the sulfides and the proper microorganisms coexist; for example, certain types of corrosion due

**Bacillus* are fast-growing, facultative species and do not produce H_2S as a consequence of their metabolism. In sufficient numbers, these could effectively compete with enteric H_2S producers characteristic of the dredged material examined in this study. Although the commercial bacterial preparations are proprietary, and hence their contents trade secrets, it is quite likely that they contain species of *Bacillus*.

to sulfate are known to be caused by the bioconversion of existing H_2S to SO_4^{-2} (Dunnette, 1973).

For the specific case of abatement of sulfidic background odors emanating from dredged materials, an investigation should be made of the feasibility of employing a soil overlay inoculated with *Thiobacillus* and/or *Beggiatoa*. If such microorganisms can be established in this layer, (the authors believe that it can be accomplished), the layer could then have the action of an active, biological filter for H_2S and perhaps other odorous sulfides. As the noxious sulfidic compounds diffuse from the lower strata through the active overlay, they would serve as substrates for sulfide-using organisms and would hence be converted to elemental sulfur or to SO_4^{-2} , thus not entering the atmosphere as a nuisance.*

The authors do not recommend consideration of the photosynthetic sulfur bacteria, since these require sunlight for their metabolism and, at best, could only act as a biofilter at the solids/air interface.

As with the other biological treatment strategies suggested in this report, laboratory studies followed by small-scale field demonstration studies must be performed to establish optimum treatment parameters on a cost-effective basis. It is concluded that although there are a number of existing or potential microbiological methods that can result in the temporary or permanent abatement of background malodors characteristic of some disposal sites, virtually none have been applied. Investigation of such microbiological methods

*It should also be noted that a mutant bacteria-containing agent ("Phenobac," Worner Biochemicals, Inc.) is commercially available which can aid the bioconversion of a number of hydrocarbons to non-noxious by-products. In view of the observation that petroleum-based odors characterize some disposal areas, the authors recommend that soil overlays containing hydrocarbon-utilizing mutants should also be investigated as a means of odor abatement.

should be made to increase the technical options for preventing or mitigating future problems with malodors.

RECOMMENDATIONS

Odor Abatement Strategy

The objective of any odor abatement strategy is to reduce the perceived intensity of malodors in the community to an acceptable level, using acceptable techniques. A plan for such a strategy was developed in the course of this project and is presented in Figure 23.

With regard to the successful abatement of malodors at diked dredged material disposal sites, there are a number of management actions that can be taken. Because malodors at these sites are not chronically severe, modest improvements at each or some of the management steps shown in Figure 23 should be valuable for reducing the possibility of malodor complaints. The results of management action or inaction, at several steps in the sequence beginning with diked disposal site selection and ending with a completely filled site, are shown in Figure 23. These actions are discussed below.

Site selection

The two most important factors for malodor abatement are (1) the distance of the diked disposal site from communities and (2) the directions of prevailing winds, especially in warm weather. As indicated in Figure 23, locating a disposal site upwind and only a short distance from dwellings will result in more complaints about malodors than will locating the site downwind and a longer distance from dwellings, especially if the site is located in an area that already has other sources of malodors.

The two most important tasks under the first step, Selection of Disposal Site (Figure 23), are thus (1) the development of wind roses for prevailing (annual) wind directions and for prevailing wind directions in warm weather, and (2) the measurement of distances to existing and planned communities for all of the potential disposal sites under consideration. Where it is possible to select a site which is a

Figure 23. Chart showing management steps for abatement of malodors.

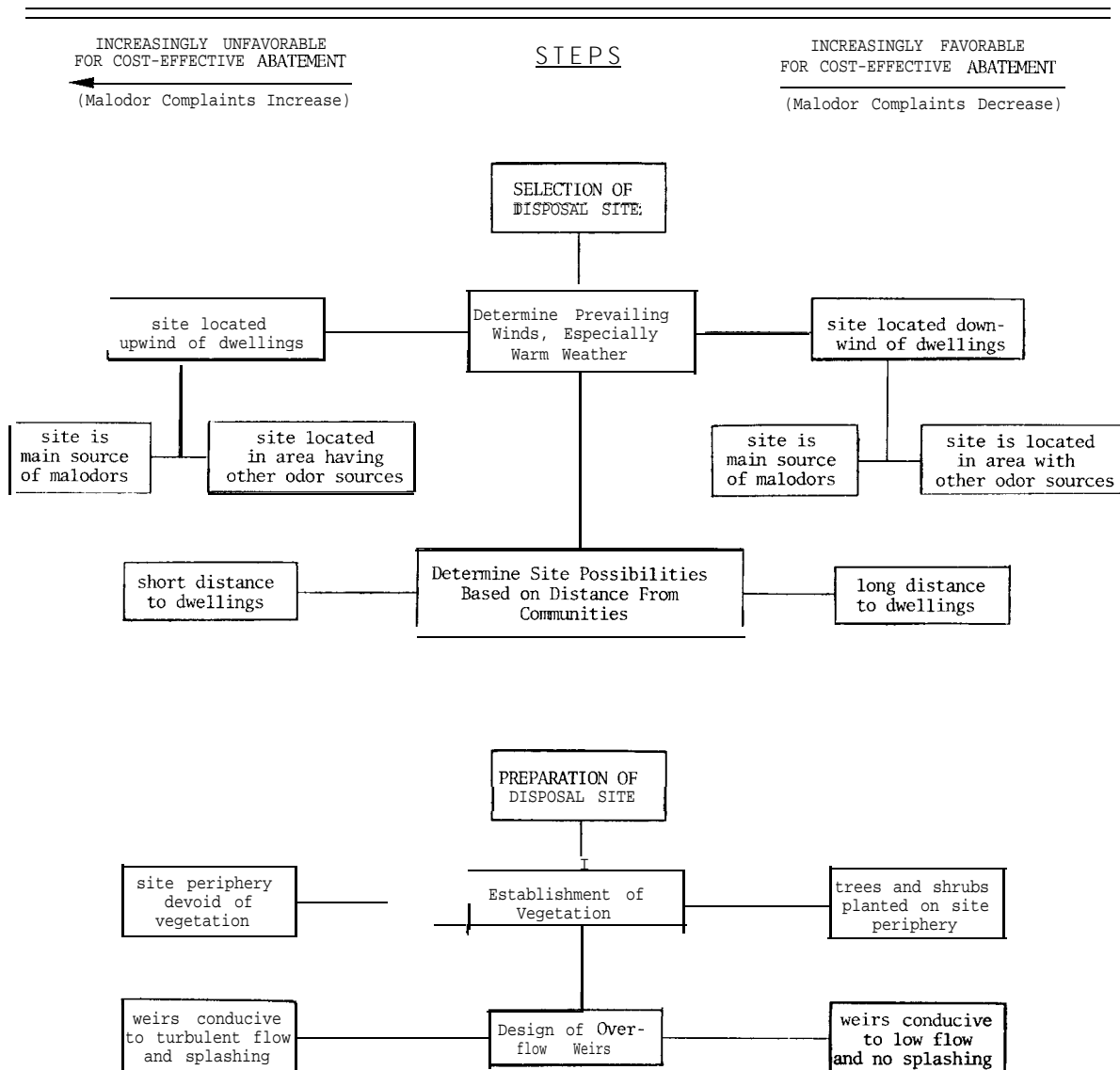


Figure 23 (Continued)

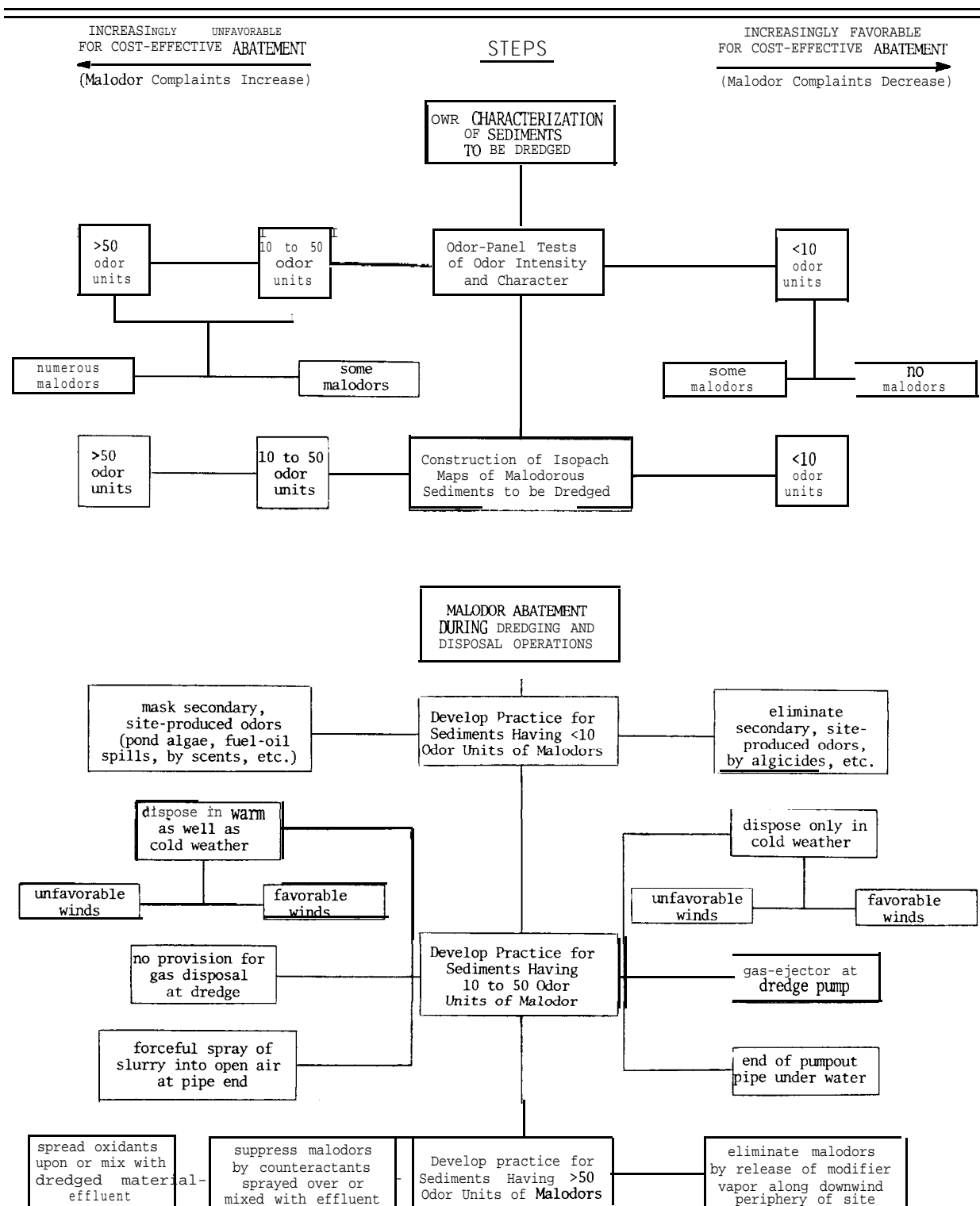
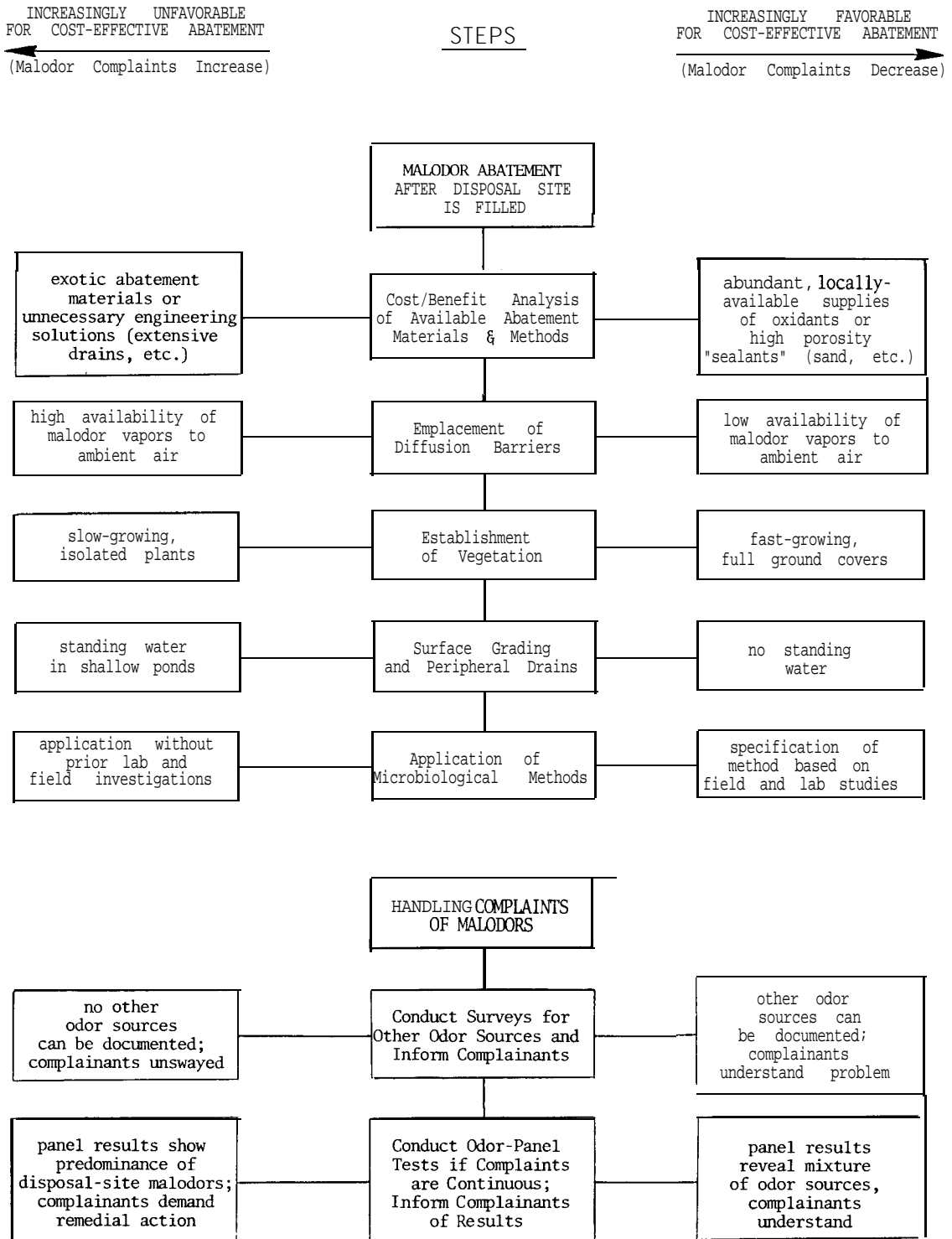


Figure 23 (Concluded)



suitably long distance from communities and is downwind of these communities during warm weather, the tasks listed next may quite possibly be ignored.

Site preparation

Planting trees and shrubs along the dike periphery will assist in increasing dispersion of malodors in the ambient air as the wind blows over the site. Similarly, the proper design of overflow weirs (see p. 17) will prevent excessive liberation of waterborne odors to the ambient air.

Odor characterization of materials to be dredged

This is an important step and should be taken whenever large volumes of potentially malodorous sediments are to be dredged. The odor tests described earlier in this report should be performed upon a sufficient number of dredged material samples to permit construction of isopach maps of units displaying odor dilution thresholds of < 10, 10 to 50, and > 50 odor units. (Isopachous maps use contours to indicate thicknesses of designated units.) These maps will allow rational decisions to be made vis-à-vis the abatement of malodors during disposal operations.

Malodor abatement during dredging and disposal operations

As shown in Figure 23, three practices should be developed. For those sediments with an ED_{50} of < 10 odor units, no special measures need to be taken other than the elimination or suppression of malodors that may be related to the dredged material disposal operation. An example would be the control of algal production in the waters within the diked area. This was a problem at the Anacortes site (p.92).

For sediments to be dredged that have ED_{50} 's between 10 and 50 odor units, a feasible practice might include any or all of the following odor-abatement approaches:

- a. Dredging and disposal only in cool weather and when the wind is blowing malodors away from the site.
- b. Installation of a gas-ejector system at the dredge pump (if a pipeline dredge).
- c. Submerging the end of the pumpout pipe under water (or otherwise enclosing the spray from the effluent stream).

When it is impossible to program dredging schedules according to weather considerations (point a., above) and still meet contract deadlines, it may be necessary to consider use of odor modifiers, counteractants, or, perhaps, oxidants.

If dredged material are malodorous, with ED_{50} 's of > 50 odor units, odor modification (p. 109) will generally be the most feasible and cost-effective approach to odor abatement. Should the volume of such sediment be a significant percentage of the total volume to be dredged and should the disposal site be close to communities, cost estimates for a suitable odor-modification system should be obtained before commencement of dredging and disposal operations. Then, in the event that the malodor problem proves unmanageable, after attempting all of the abatement procedures mentioned above, it will be possible to move quickly. The use of odor modifiers is recommended in preference to odor counteractants and masking agents for reasons given earlier. The use of oxidants to destroy odors at the source (that is, within the dredged material) is an intriguing approach to abatement, but as yet entirely unproven as to its reliability or cost effectiveness for short-term abatement of malodors. The use of oxidants for long-term abatement may be more realistic.

Malodor abatement after filling of site

To be cost effective, the long-term abatement of malodors should use minimum amounts of abatement materials consistent with reducing residual malodors to an acceptable level. In general, locally available material, such as lime; hydrogen sulfide removers, such as ferrous sulfate (U.S. Environmental Protection Agency, 1972); sealants, such as sand; or diffusion barriers, such as wood chips, are to be preferred to their more expensive counterparts. Finally, a number of strategies involving microbial methods, discussed elsewhere in this report, may result in cost-effective, long-term abatement of malodors.

The emission of malodors from a filled site can be reduced by cluttering the surface with some form of material that is either a film which acts as a diffusion barrier for odorants, or is fibrous and immobilizes turbulence and eddy currents in the ambient air above the surface of the dredged material. The latter approach effectively increases the thickness of the stagnant diffusion region in the air at the surface. Above the surface, in the region of eddy currents, the formal diffusion coefficient is 10^4 to 10^5 higher than in the stagnant boundary layer.

Handling complaints

Other odor sources may emit malodors that people mistakenly assign to the disposal of dredged material. Three such cases were observed during the seven field trips. In Milwaukee, odors from the municipal sewage disposal plant produced a plume that sometimes crossed the odor plume from the hopper dredge. In Mobile, a significant mal-odor was emitted from Chicksaw Creek where discharges from a nearby paper mill entered the stream. In Houston, during a walking trip through an adjoining housing development, strong odor was experienced toward the end of a street ending at the disposal site dike. A closer inspection revealed that this odor came from a garbage pile at the

end of the street. Thus, an odor complaint may be assigned mistakenly to the dredged material. It may be useful to survey the area around a diked site for alternate odor sources and to analyze complaints by onsite inspections for the possible contributions of other sources. Gas leaks are one type of source to be considered.

In those instances where complaints of malodors from a disposal site persist, it may be necessary to obtain the services of an odor panel. Documentation of the community odor profile and interpretation of the odor-panel results by a trained odor consultant, permits development of a rational response to complaints. If the odor-panel results and their interpretations indicate a significant problem at the site, as opposed to malodors originating from other sources in the area, one or more of the remedial measures described in the two preceding sections will be required.

Demonstration Projects

Finally, the authors recommend that the various diked disposal site demonstration projects, currently being supervised by the Dredged Material Research Program, be used wherever possible to examine the feasibility of the odor-abatement procedures discussed above. A series of experiments could be developed to test the odor-abatement value of oxidants, diffusion barriers, vegetation, bacterial strategies, and other abatement techniques. It would be especially useful to have a test of an odor-modification system and to compare its cost effectiveness with other methods at a disposal site where malodors are a chronic problem.

It has been said (Lauren and Gilbertsen, 1975) that odor modification is the only economically feasible way of abating malodors from area sources. This approach seems promising in view of the minimal capital and operating costs involved and should be thoroughly tested.

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APPENDIX A: THE SULFUR CYCLE IN THE HYDROSPHERE

In view of the prevalence of sulfidic odors* at a number of the disposal sites visited, and because there appear to be several similarities between the biogenesis of sulfur-containing compounds in the dredged materials and that in the sediments of the hydrosphere, and since a considerable amount of information is available concerning this cycle, a discussion of the sulfur cycle in the hydrosphere is in order.

In the hydrosphere, including sediments, the most common substrates for hydrogen sulfide (H₂S) are sulfate ion and organic matter.

In most fresh waters, sulfate is the second or third most common anion (Hutchinson, 1957)** exceeded only by biocarbonate and, in some water bodies, by silicate. In brackish or sea water its relative abundance is less due to the presence of anions such as chloride. The principal sources of sulfate are precipitation and, in freshwater lakes and rivers, runoff. Other common sources include submerged sedimentary rocks containing calcium sulfate or pyrites.

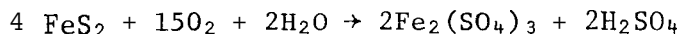
Organic material in sediments is derived from the settling of lifeless aquatic plant and animal debris (e.g., water plants, algae, plankton, fish, etc.), or from accessory debris (sewage plant wastes, industrial wastes, dead waterfowl, insects, waterfowl feces, etc.).

Figure A-1 depicts the sulfur cycle in the hydrosphere, and summarizes the physical and microbial events that lead to the production of H₂S (and other sulfur-containing compounds) in sediments. The sulfate ion, one of the principal substrates for the production of H₂S, enters the sulfur cycle from the atmosphere via precipitation,

*Especially hydrogen sulfide and diethylsulfide.

**References in the appendix are given in the "References" section following the main text.

† Pyrites can oxidize, yielding the sulfate ion, as follows:



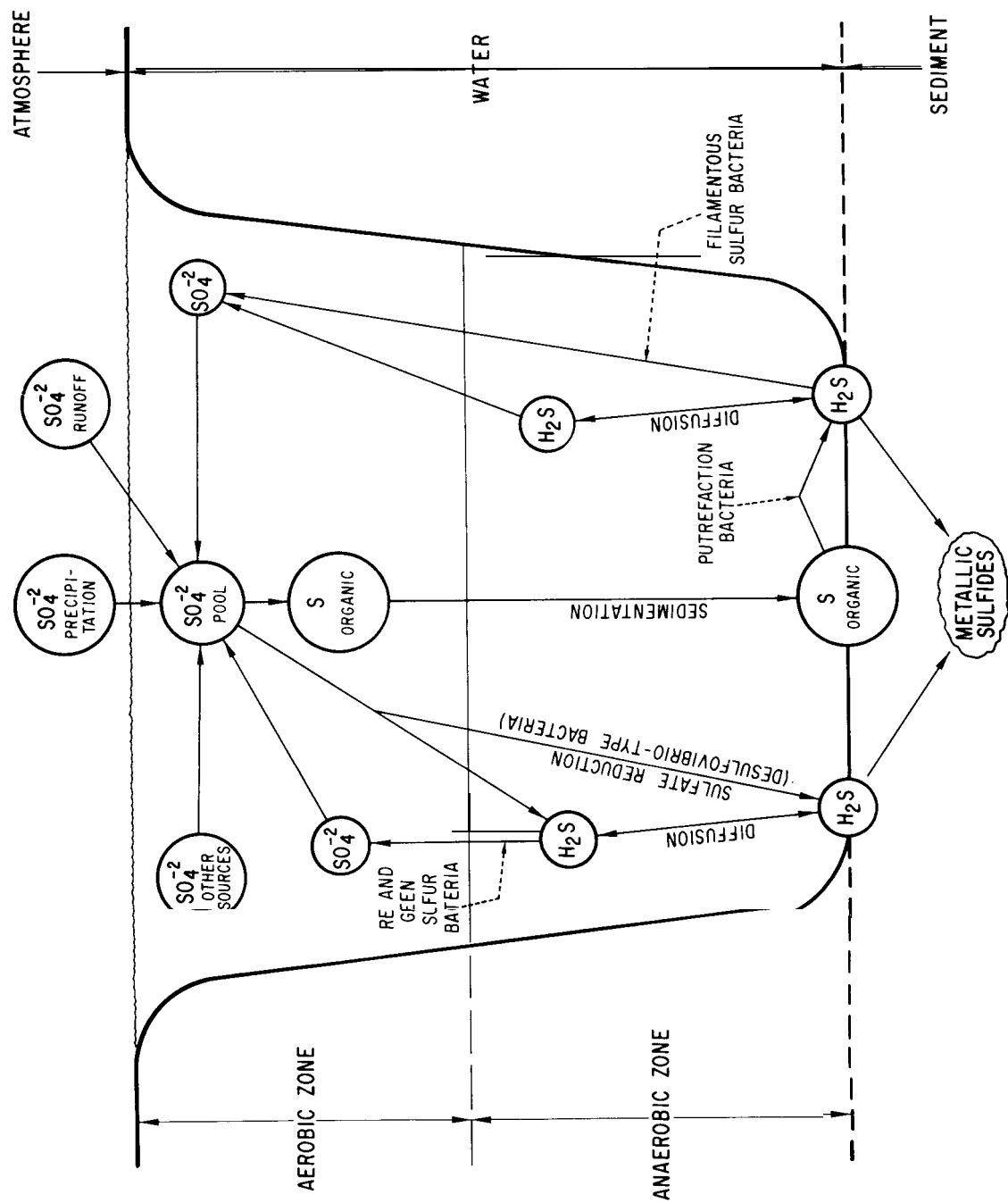


Figure A-1. Sulfur cycle in the hydrosphere (modified from

1971, and Dunette, 1973).

from the land as runoff, from less universal sources (indicated as "other sources" on Figure A-1) such as dilute sulfuric acid streams in the vicinity of volcanic areas, mineral streams, and mining areas, and as a result of the conversion of existing H_2S to sulfate ion. While a fraction of the sulfate ion is directly acted upon by microorganisms (i.e., *Desulfovibrio* sp.) to yield H_2S , much of the remainder is first incorporated into the sulfur-containing amino acids and proteins of biota that eventually die and enter the sediment phase as organic material. Here, other types of organisms, usually anaerobic species such as *Clostridia*, act upon the sulfur-containing molecules of this and other organic matter to produce H_2S . While some of the H_2S remains in this chemical form in the sediments and, in some cases, in anaerobic strata of the water column above the sediments, the remainder may be immobilized in the form of metallic sulfides (e.g., FeS_2), or may be acted upon by additional bacterial species that oxidize H_2S to regenerate elemental sulfur or sulfate.

In the above scheme, the authors believe that it is the H_2S contained in the sediments or water column that is likely either to be instantaneously available as an **odorant** at the time of discharge of dredged materials at disposal sites or to be eventually brought to the surface of disposal areas to enter the atmosphere at a later time. Similarly, the dredged organic material is likely to be the major substrate for bacterial action in the disposal beds for the production of H_2S and other sulfur-containing organic compounds as diethylsulfide, other organic sulfides, and the mercaptans. Organic material is also likely to serve as a substrate for bacterial gas production (p. 74ff). Finally, dredged metallic sulfides could themselves conceivably contribute H_2S to the atmosphere of the disposal sites under appropriate physical conditions (low pH), or by the action of bacteria.

APPENDIX B. NOTATION

Ca(OH)_2	calcium hydroxide
D/T	dilution-to-threshold ratio as defined in Scentometer manual
DVB	<i>Desulfovibrio</i> agar medium
ED ₅₀	odor dilution threshold
FeS_2	iron disulfide
$\text{Fe}_2(\text{SO}_4)_3$	iron (III) sulfate
GC/MS	gas chromatograph/mass spectrometer
Gp	group
GRAS	Generally recognized as safe
H_2O_2	hydrogen peroxide
H_2SO_4	sulfuric acid
H_3PO_4	orthophosphoric acid
KMnO_4	potassium permanganate
m/e	mass to charge ratio in mass spectrometry
NaOCl	sodium hypochlorite
O_3	ozone
o.u.	odor unit
p	statistical probability
SO_4	sulfuric ion
z	a statistical value measuring the difference between mean values of sample groups

In accordance with ER 70-2-3, paragraph 6c(1)(b),
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Harrison, W

Abatement of malodors at confined dredged material disposal sites, by W. Harrison, A. Dravnieks, R. Zussman, and R. Goltz, Argonne National Laboratory, Argonne, Illinois. Vicksburg, U. S. Army Engineer Waterways Experiment Station, 1976.

145 p. illus. 27 cm. (U. s. Waterways Experiment Station. Contract report D-76-9)

Prepared for Office, Chief of Engineers, U. S. Army, Washington, D. C., under Interagency Agreement No. WESRF 75-104; (DMRP Work Unit No. 2C11)

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TA7.W34c no. D-76-9